Old Dominion University Research Foundation

DEPARTMENT OF MECHANICAL ENGINEERING AND MECHANICS
COLLEGE OF ENGINEERING AND TECHNOLOGY
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA 23529

DETERMINATIONS OF MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF HIGH POLYMERS BY THE RHEOLOGICAL PROPERTIES

82 P

By

J. Y. Huang, Graduate Research Assistant

T. H. Hou, Adjunct Assistant Professor

and

S. N. Tiwari, Principal Investigator

Progress Report
For the period ended June 30, 1989

Prepared for
National Aeronautics and Space Administration
Langley Research Center
Hampton, VA 23665

Under
Research Grant NAG-1-569
Robert M. Baucom, Technical Monitor
MD-Polymeric Materials Branch

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FOREWORD

This is a progress report on the research project, "Chemoviscosity Modeling for Thermosetting Resins," for the period ended June 30, 1989. Special attention during this period was directed to "Determinations of Molecular Weight and Molecular Weight Distribution of High Polymers by the Rheological Properties." The work was supported by the NASA Langley Research Center (Polymeric Materials Branch of the Materials Division) under the grant NAG-1-569. The grant was monitored by Mr. Robert M. Baucom of the MD-Polymeric Materials Branch, Mail Stop 226.

DETERMINATIONS OF MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF HIGH POLYMERS BY THE RHEOLOGICAL PROPERTIES

By

J.Y. Huang[1], T.H. Hou[2], and S.N. Tiwari[3]

SUMMARY

Several methods are reviewed by which the molecular weight (MW) and molecular weight distribution (MWD) of polymeric material were determined from the rheological properties. A poly(arylene ether) polymer with six different molecular weights was used in this investigation. Experimentally measured MW and MWD were conducted by GPC/LALLS (Gel Permeation Chromatography/Low Angle Laser Light Scattering), and the rheological properties of the melts were measured by a Rheometric System Four rheometer. It was found that qualitative information of the MW and MWD of these polymers could be derived from the viscoelastic properties, with the methods proposed by Zeichner and Patel, and by Dormier et al., by shifting the master curves of the dynamic storage modulus, G′, and the loss modulus, G", along the frequency axis. Efforts were also made to calculate quantitative profiles of MW and MWD for these polymers from their rheological properties. The technique recently proposed by Wu was evaluated. It was found that satisfactory results could only be obtained for polymers with single modal distribution in the molecular weight.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

a_m	shift factor related to molecular weight ratios
a_T	shift factor of WLF
B	numerical constant used in Eq. (5.3b)
C	numerical constant used in Eq. (5.3b)
C_1	temperature-dependent parameter
C_2	temperature-dependent parameter
$D(\tau)$	weight-fraction differential molecular weight distribution function
G_j^o	numerical constant
Gn^o	plateau modulus
GPC	gel permeation chromatography
$G(t)$	stress relaxation modulus
$G'(\omega)$	dynamic storage modulus
$G''(\omega)$	dynamic loss modulus
$H(\tau)$	relaxation time spectrum
Je^o	steady state creep compliance
Mc	critical molecular weight
Mn	number average molecular weight
Mr	relative molecular weight
MW	molecular weight
MWD	molecular weight distribution
Mw	weight average molecular weight
Mw/Mn	polydispersity ratio

Mz	z average molecular weight
PAE	poly(arylene ether)
P(M)	volume-fraction differential molecular weight distribution function
P	odd integer
$R_{\bar{\theta}}$	excess Rayleigh factor
S	scaling factor
T	temperature
T_c	reference temperature
WLF	Williams-Landel-Ferry

Greek Letter

α_j	numerical constant
β	constant
η_o	zero shear viscosity
η^*	complex viscosity
λ	constant
τ	relaxation time
τ_j	numerical constant
ω	frequency
ω_R	reduced frequency

Chapter 1

INTRODUCTION

High performance thermoplastics have received considerable attention recently in the aerospace industry for their potential use as structural resins. These materials possess an attractive combination of chemical, physical and mechanical properties. Changes in molecular weight (MW) and molecular weight distribution (MWD) are responsible for many of the properties of polymers. For example, the toughness of the high performance polymers is related to the dynamic moduli G' and G", which are related to MW and MWD. Therefore, the determination of MW and MWD of these high performance polymers become an important analytical problem in research and in process control. Traditional methods for molecular weight determination are solution techniques such as light scattering and gel permeation chromatography (GPC) methods.

Applying the traditional methods to determine the molecular weight of a polymer, the polymer must be soluble in a suitable solvent. However, most of the high performance polymers are insoluble. Therefore, the molecular weight and molecular weight distribution of these polymers cannot be determined readily by traditional methods.

It is well established that rheological measurement can be very sensitive to MW and MWD. Thus, rheological properties can in principle be used to deduce the MW and MWD of polymers. For linear viscoelastic materials, many of the rheological functions can be expressed in terms

of a suitably defined relaxation spectrum. It is logical to suppose that this relaxation spectrum is associated with a corresponding spectrum of molecular response times, which in turn is a function of molecular size, shape, etc. The quantity used to describe the MW and the MWD of a polymer is the weight average molecular weight (Mw), the number average molecular weight (Mn) and the polydispersity ratio (Mw/Mn).

Only a few empirical methods have been proposed during the past two decades for predicting the polymer MW and MWD by rheological properties. A fundamental understanding of these methods has been necessary in order to develop and apply these methods to insoluble high performance polymers.

The objective of the present study is to investigate several empirical methods by which the polymer MW and MWD can be determined by rheological properties. A high performance thermoplastic polymer, poly(arylene ether), is used to evaluate these methods. The MW and MWD calculated are compared with experimental data.

A short literature survey is given in Chap. 2. The experimental methods are described in Chap. 3. The theory of empirical methods are discussed in Chaps. 4 and 5. A comparison between the theoretical and experimental results is given in Chap. 6.

Chapter 2

LITERATURE SURVEY

The various zone of viscoelastic behavior for uncross-linked polymers of high molecular weight is shown in Fig. 2.1, where G' is the dynamic storage (elastic) modulus and G" is the loss modulus. The viscoelastic functions of G" and G' in these zones have characteristic shapes: the transition zone from glasslike to rubberlike consistency, the plateau zone where G' changes only slightly with frequency, and the terminal zone. These regions can be associated qualitatively with different kinds of molecular responses. The portion of the master curve which is experimentally accessible lies in the terminal zone. Molecular weight and molecular weight distribution strongly influence the frequency dependence of the dynamic moduli in the terminal zone.

For linear viscoelastic response, the elastic and loss moduli, G' and G", are related to the zero-shear viscosity, η_0, and the steady state creep compliance, Je^o as follows:

$$\lim_{\omega \to 0} \frac{G''}{\omega} = \eta_o$$

$$\lim_{\omega \to 0} \frac{G^1}{\omega^2} = \eta_o^2 \, Je^o$$

For linear polymers with high molecular weight, Je^o is independent of Mw, but strongly dependent on molecular weight distribution. Based on these expressions, an empirical technique is proposed by Zeichner and

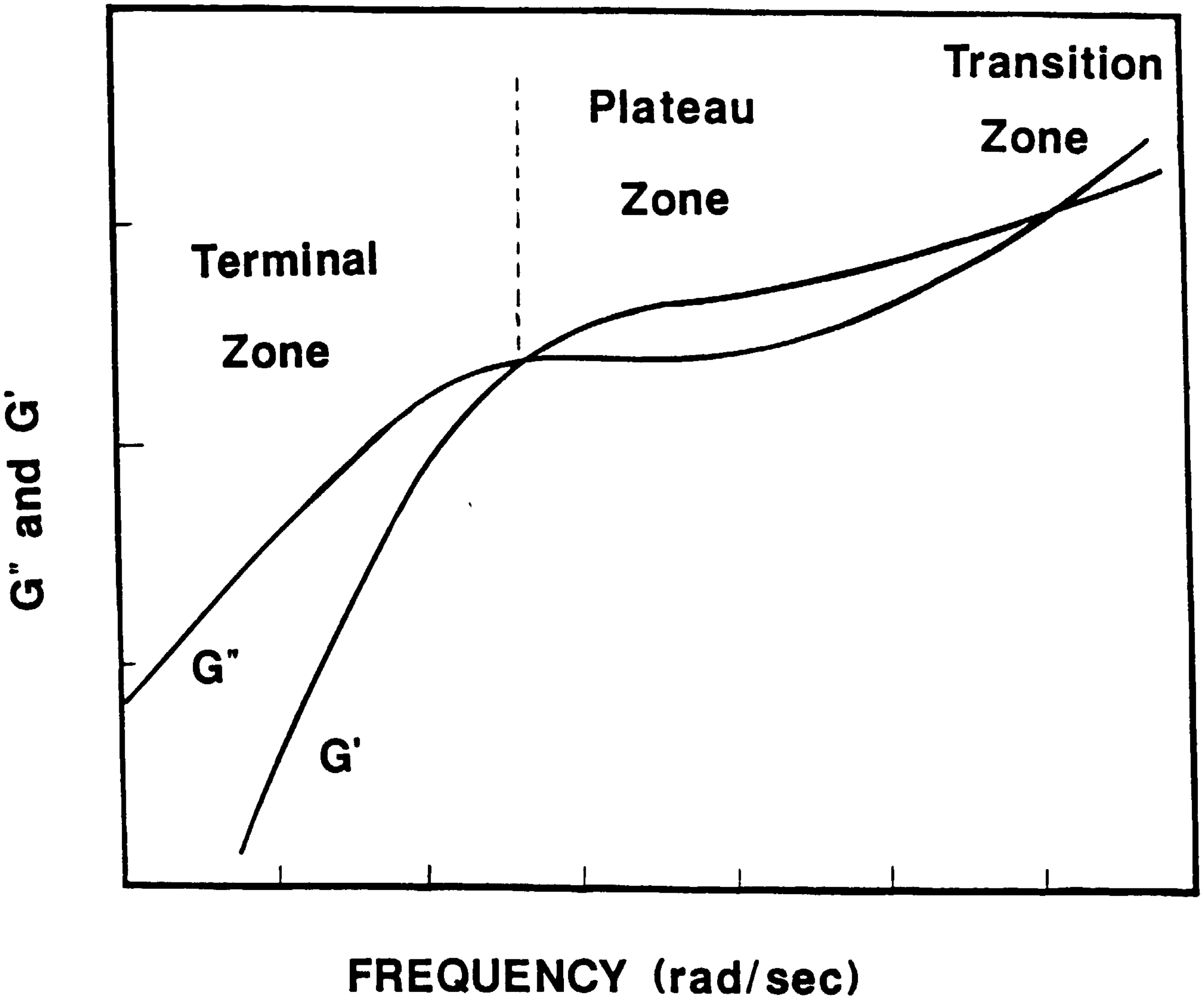

Fig. 2.1 Various zone of viscoelastic behavior for uncross-linked polymers of high molecular weight.

Patel [1]* to obtain the MW and MWD qualitatively. A reduced frequency $\omega_R = \eta_o\omega$, was defined to eliminate the differences of viscosity and molecular weight between polymers of same molecular weight distributions. By plotting the dynamic moduli G' and G" data along the reduced frequency axis, all G" data of polymers in the low frequency region will superimpose irrespective of individual material's molecular weight and molecular weight distribution. All G' data on the other hand, will be superimposable to form a master curve independent of molecular weight provided that molecular weight distribution is fixed. The method was illustrated by a series of polypropylene polymers [1]. The correlation obtained was illustrated in Fig. 2.2, where reduced master curves for broad and narrow molecular weight distribution polypropylenes were compared.

In a similar manner, a method for interpreting dynamic rheological data to characterize MWD was proposed by Dormier, Tong and Lagasse [3]. Master curves of dynamic moduli G' and G" of two different types of polymers were shifted along the frequency axis to obtain superposition of G" data at the terminal zone. By this treatment, visual inspection of the shifted curves would give qualitative MWD information, and the magnitude of the shift factor would yield a quantitative measurement of Mw. The relation between Mw and shift factor can be expresses as:

$$(Mw)_h/(Mw)_l = (a_m)^{1/3.4} \qquad (2.1)$$

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*The numbers in brackets indicate references.

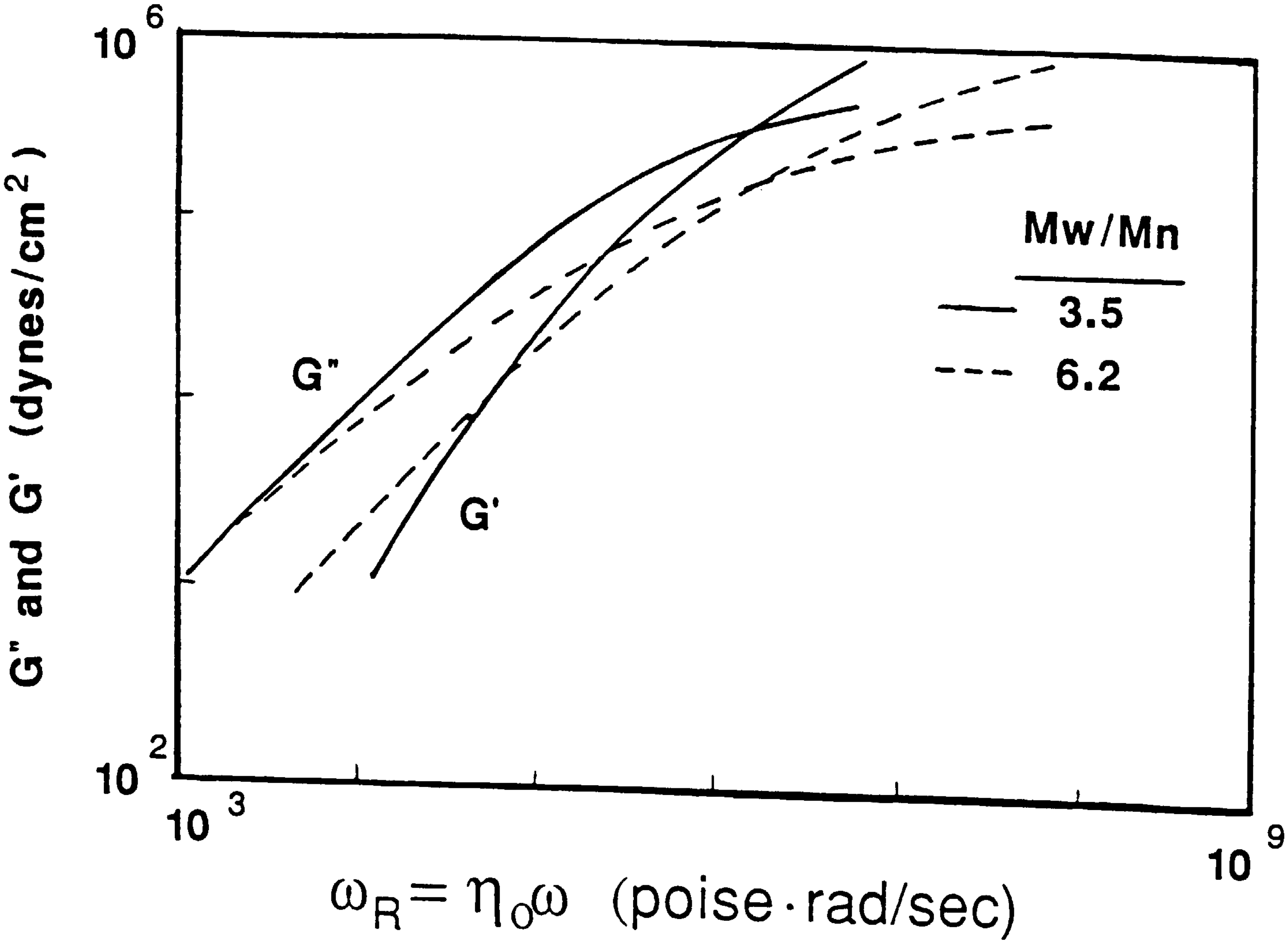


Fig. 2.2 Reduced master curves for broad and narrow MWD polypropylenes.

where, $(Mw)_h$ and $(Mw)_l$ denoted the higher and lower molecular weight of the two different polymers. The ratio 3.4 comes from the relationship $\eta_0 \propto Mw^{3.4}$, which was found valid for many linear polymers with flexible backbone chains. By shifting the master curves to overlap G" at low frequencies, a qualitative measure of molecular weight distribution could be obtained by comparing the magnitude and the slope of G'. As Dormier, Tong and Lagasse [3] pointed out that this technique is sensitive to the high molecular weight tail and can be used to distinguish similar resins.

The first attempts at quantitatively calculating a MWD curve from rheological data were made by Ninomiya and Fujita [4, 5]. They related the relaxation spectrum of linear amorphous polymers to the normalized weight distribution of molecular weights in a linearly additive manner.

The differential molecular weight distribution function deduced by Ninomiya and Fujita is expressed as

$$\phi\ (Mm) = -\frac{2.303}{\bar{E}\ Mc} \log\ (\frac{\tau}{\tau_e}) \frac{\log\ (\tau/\tau_e)}{d(Mm/Mc)} \frac{d\Phi(\log\tau)}{d\ \log\ \tau} \qquad (2.2)$$

where, $\bar{E}$ is the relaxation modulus, Mc the critical molecular weight and τ the relaxation time. This theory was developed on the assumption that the relaxation spectrum of a perfect monodisperse polymer in the rubbery consistency can be approximated by a box-shaped function as shown in Fig. 2.3. The fair agreement was obtained by comparing the MWD curve obtained by this method with the one obtained by fractionation procedures for polystyrene and polyvinyl [4]. But the curve was dissimilar in the low molecular weight regions. The method is useful for estimates of a MWD curve, the over-all spreading, the maximum height, and its location on the molecular weight axis. It was confirmed

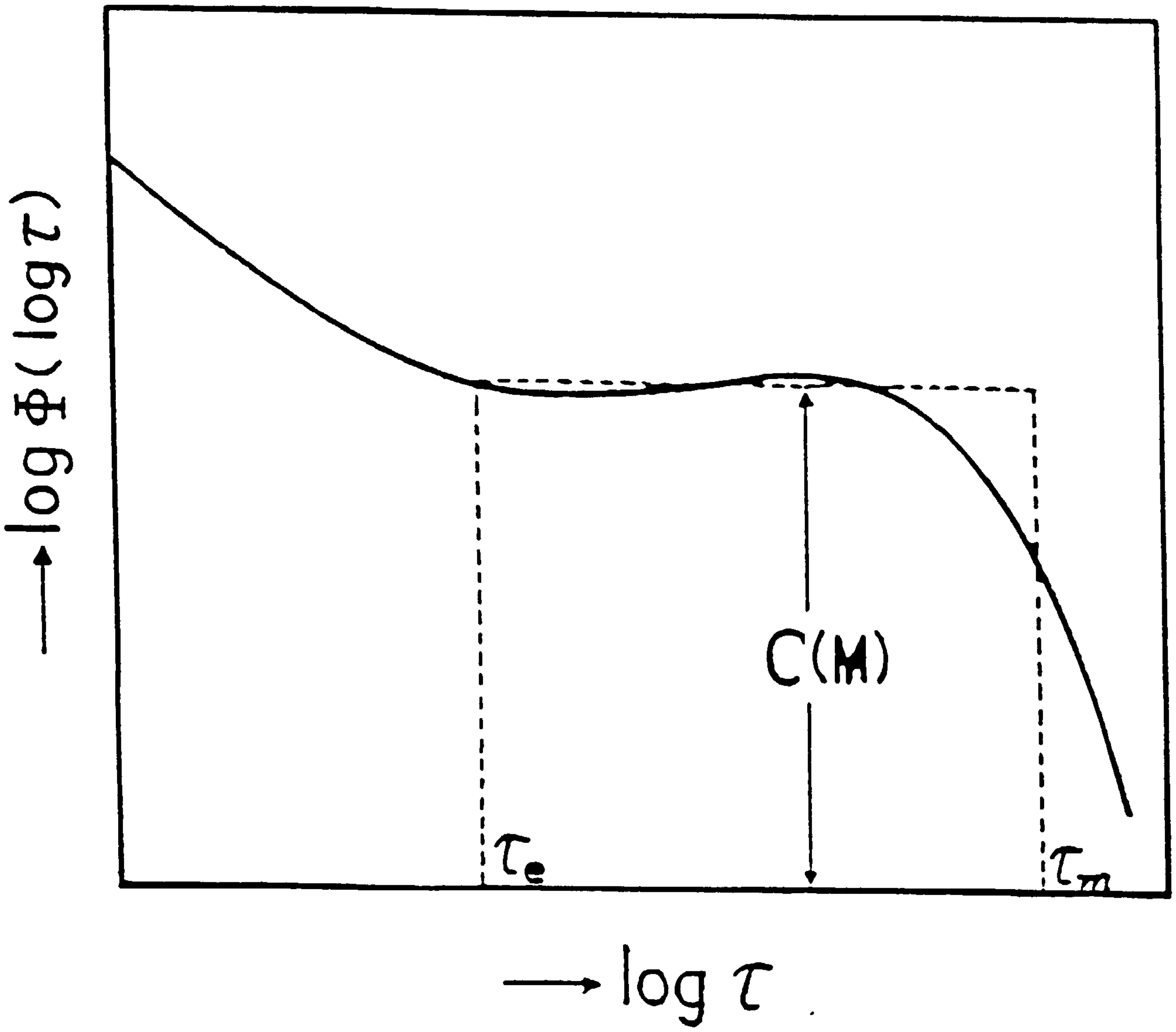


Fig. 2.3 Schematic diagram of the relaxation spectrum of a linear amorphous polymer in the rubbery region, where the actual spectrum is approximated by a box-type function.

that the shape and width of the relaxation spectrum in the rubbery consistency of a linear amorphous polymer is quantitatively correlated with the weight distribution of molecular weights.

Recently, a method was developed by Wu [6] to make the MW and MWD calculations by deconvoluting the dynamic rheological properties in the terminal and plateau zones. The method is based on the development of rheological constitutive equations by Doi and Edwards [7]. The dynamic storage modulus G' and the stress relaxation modulus G(t) in terminal and plateau zones contains a spectrum of molecular relaxation times, which can be deconvoluted to obtain the molecular weight distribution curve.

Based on Doi-Edwards theory, the linear viscoelastic storage modulus for a polydisperse polymer with continuous molecular weight ditribution can be expressed [6] as,

$$G'(\omega) = \int_{-\infty}^{\omega} D(\tau) \frac{8}{\pi^2} Gn^o \sum_{\text{oddp}} \left(\frac{1}{p^2}\right) \frac{(\omega\tau/p^2)}{1 + (\omega\tau/p^2)^2} \, d \ln \tau \qquad (2.3)$$

where $G'(\omega)$ is the dynamic storage modulus, which is frequency dependent, τ the longest relaxation time, $D(\tau)$ is the weight-fraction differential molecular weight distribution function and Gn^o is the plateau modulus. The solution of $D(\tau)$ was obtained by either inverting the above integral or calculating the approximate first-order derivative. An empirical expression for G' was proposed in order to solve for $D(\tau)$ from Eq. (2.3). This method was applied to predict the MW and MWD for a series of monodisperse (narrow distribution) and polydisperse (broad distribution) polystyrenes with the assumption that the cumulative MWD is proportional to (G'/Gn^o). The results of Mw, Mn and Mw/Mn were found to agree with the experimental data within 10 percent.

Tuminello [8] improved Wu's method and applied it to some polymers that have bimodal molecular weight distributions. It was suggested that for bimodal distributions, the accumulative MWD is approximately proportional to (G'/G_n^0). The results for Mw, Mn and Mw/Mn obtained for bimodal blends of polystyrene agreed quite closely with experimental results.

Later, Wu extended his method to the case of using stress relaxation modulus to predict molecular weight and molecular weight distribution [9, 10]. The linear viscoelastic stress relaxation modulus of a polydisperse whole polymer was given by

$$G(t) = \int_{-\infty}^{\infty} G_n^0 \, H(\tau) \exp(-t/\tau) \, d \ln \tau \qquad (2.4)$$

where $G(t)$ is the stress relaxation modulus at time t, $H(\tau)$ is the relaxation time spectrum, τ the relaxation time for a monodisperse species in the polydisperse blend, and G_n^0 the plateau modulus. The volume-fraction differential molecular-weight distribution function was given by

$$P(M) = \frac{1/\sqrt{2}\ H(M)}{[\int_{\ln M}^{\infty} H(M)\ d \ln M]^{1/2}} \qquad (2.5a)$$

or

$$P(M) = \frac{1/\sqrt{2}\ H(M)}{2.303\ [\int_{2.303 \log M}^{\infty} H(M) \log M]^{1/2}} \qquad (2.5b)$$

Wu applied this method on a number of polystyrenes and poly(tetrafluoroethylenes), PTFEs. Usually, PTFEs have broad and bimodal molecular weight distributions. The number average molecular weight Mn obtained by this method agreed fairly with the one determined

by end group method for PTFEs [9]. The results for polystyrenes was good with discrepancies generally less than 5 to 10% [10].

Chapter 3

EXPERIMENTAL METHODS

3.1 Light Scattering Measurement

Light scattering occurs whenever a beam of light encounters matter. The nuclei and electrons undergo induced vibrations in phase with the incident light wave and act as sources of light that is propagated in all directions, aside from a polarization effect, with the wave length as the exciting beam. The amplitude of the scattered light is proportional to the polarizability and hence to the mass of the scattering particle.

The poly(arylene ether ketone) samples were dissolved in Gold Label Chloroform. The instrument used to performed the absolute weight average molecular weight Mw is the Chromatrix KMX-6 Low Angle Laser Light Scattering Photometer, which is a versatile tool for the polymer characterization laboratory. Samples were measured under static mode to obtain the absolute weight average molecular weight Mw. With the unique optical design and use of a laser light source, the scattered light from a small scattering volume (0.1 microliter) was collected at a low angle to the incident beam. Sample clarification is very important in the measurement, since a dust particle could be much bigger than polymer molecules, thus to influence the result. The accuracy of molecular weight determinations by light scattering is dependent on the accuracy of the differential refractive index measurement, which is accomplished

by measuring the deviation of a light beam passing through a divided cell composed of adjacent solvent and solution compartments. Molecular weights were obtained from a simple measurement of concentration dependence of the sample scattering.

3.2 GPC/LALLs Measurement

Gel permeation chromatography (GPC) is a technique for the separation and characterization of polymers according to molecular sizes. It does not directly provide molecular weight data. The separation takes place in a chromatographic column filled with beads of a rigid porous "gel." Highly cross-linked porous polystyrene and porous glass are preferred column-packing materials. The pores in these gels are of the same size as the dimension of polymer molecules. A sample of a dilute polymer solution is introduced into a solvent stream flowing through the column. As the dissolved polymer molecules flow past the porous beads, they can diffuse into the internal pore structure of the gel to an extent depending on their size and the pore-size distribution of the gel. Larger molecules can enter only a small fraction of the internal portion of the gel, or are completely excluded; smaller polymer molecules penetrate a larger fraction of the interior of the gel. The larger the molecule, therefore, the less time it spends inside the gel, and the sooner it flow through the column. The different molecular species are eluted from the column in order of their molecular size as distinguished from their molecular weight, the largest emerging first.

KMX-6 connected in series with the gel permeation chromatographic columns and a conventional concentration-sensitive GPC detector was used in GPC measurement. PAE samples were dissolved in Gold Label

chloroform. Each sample was analyzed at least three times. To avoid excessive back pressure on the GPC detector cells, the light scattering cell was connected between the column and the GPC detector. The molecular distribution was then calculated directly from the KMX-6 measurement of the excess Rayleigh factor, $R_{\bar{\theta}}$, the GPC detector response, and two polymer constants, which are the specific refractive index increment and the second virial coefficient.

3.3 Rheological Measurements

3.3.1 Sample Preparation

A sample disc of 2.50 cm in diameter was prepared by molding 0.7 g of material at 250°C under a pressure of 200 psi. Lower pressure was necessary when some samples with lower molecular weights were molded. The resulting disc was approximately 1.5 mm in thickness and was transparent with light brownish color. The prepared sample discs were pre-dried in an oven at 100°C for at least 24 hours and removed just prior to the measurement.

3.3.2 Apparatus

The Rheometric System Four was used in rheological measurements. This system is an automated laboratory instrument for characterizing the rheological properties of a broad range of materials. It is a modular designed system of four independent servos linked to a common computer system for control and data analysis.

When the mode, temperature and deformation history is selected, the computer translates the strain or shear rate history into motion of the servo motor based on the test geometry in use. Sample temperature is

controlled during the test with a convected gas environmental chamber. The torque and normal force generated in response to the imposed motion is measured by a transducer. The computer calculates stresses from the torque and normal force measurements and combines these values with measured sample motion to calculate values of the selected rheological properties. The computer and associated electronics provide precision control and rapid data analysis with results conveniently plotted and printed in graph and tabular form.

3.3.3 Calibration

The Rheometric System Four calibration include transducer normal and torque calibration, temperature calibration and phase calibration. All calibrations were performed by following the procedure recommended by the manufacturer [23].

The transducer normal and torque calibration is to adjust the normal and the torque to ensure the accuracy of the test results.

The temperature calibration is divided into three parts as follows: oven thermocouple calibration; fluid bath thermocouple calibration and oven PRT set point. Thermocouple calibration was performed using a thermometer as a reference. The PRT set point was calibrated using the thermocouple as a reference.

The torque phase calibration was accomplished to compensate for phase shift in the electronics. Calibration was performed with dynamic motor in TORSION RECT using an elastic material such as steel for a phase angle of zero degree.

3.3.4 Measurements of Rheological Properties

The rheological properties G' and G" were measured under dynamic, rate sweep mode. Parallel-plates configuration was used in all experiments. Measurements were made at different strain to ensure the responses were in the linear viscoelastic region. Measurement temperature ranged from 160°C to 280°C in a dry nitrogen atmosphere.

The storage modulus $G'(\omega)$ is a measure of stored elastic energy, and the loss modulus $G''(\omega)$ is a measure of the energy dissipated or lost. They are calculated by the Rheometrics supplied Data Acquisition and Analysis package.

Chapter 4

QUALITATIVE ANALYSIS METHODS

The rheological behavior of a polymeric material in the low frequency region or terminal zone is generally characterized by the zero shear viscosity, η_0, and the steady state compliance, Je^o, which are defined as follows:

$$\lim_{\omega \to 0} G'' = \eta_o \omega \qquad (4.1)$$

and

$$\lim_{\omega \to 0} G' = \eta_o^2 \, Je^o \, \omega^2 \qquad (4.2)$$

Blending rules for linear viscoelastic response relate η_0 to Mw and Je^o to ratios of higher moments such as polydispersity ratio Mw/Mn, therefore relate G' and G" to MW and MWD as well. Analyzing the data of dynamic moduli G' and G" in low frequency region will give qualitative information about MW and MWD.

4.1 Method of Zeichner and Patel

Since G" is related to the zero shear viscosity and G' is related to the shear compliance Je^o, therefore the master curve of G" and G' will relate to molecular weight and molecular weight distribution respectively. A reduced variable was introduced by Zeichner and Patel to Eliminate viscosity and molecular weight differences between polymers of like MWD. The reduced frequency ω_R was defined as $\omega_R = \eta_o \omega$. By

shifting the G" and the G' master curves along the reduced frequency axis, the data of G" and G' for polymers have identical molecular weight distribution will superimpose irrespective of their molecular weight. For polymers having different molecular weight distribution, by overlapping the G" curve at low frequency limit, the G" and G' curve will have different slope.

4.2 Method of Dormier, Tong and Lagasse

The empirical method proposed by Dormier, Tong and Lagasse [3] is by shifting the G' and G" master curves of two different polymers along the frequency axis to obtain the superposition on G" at the lowest frequency limit. This treatment was chosen because usually for broad distribution polymers G" reaches its limiting slope at higher frequencies than G'. Also in light of the dependence of G" on η_0 in the low frequency limit, this shifting procedure removes the effect of differences in η_0 (i.e. Mw). The relation suggested between Mw and the shifting factor is

$$(Mw)_h/(Mw)_1 = a_m^{1/3.4} \qquad (4.3)$$

where $(Mw)_h$ and $(Mw)_1$ indicate the higher and the lower molecular weight of two different polymers. The shift factor a_m is obtained by shifting the G" curve of higher Mw sample to G" curve of the lower molecular weight one. The index 3.4 comes from the theory that for most polymers the following relation is satisfied [18]

$$\eta_0 \propto Mw^{3.4} \qquad (4.4)$$

Since the shift factor corresponds exactly to the ratio of the zero shear viscosities,

$$\frac{\eta_h}{\eta_1} = \frac{(M_w)_h^{3.4}}{(M_w)_1^{3.4}} = a_m$$

therefore,

$$\left(\frac{\eta_h}{\eta_1}\right)^{1/3.4} = \frac{(Mw)_h}{(M_w)_1} = a_m^{1/3.4} \qquad (4.5)$$

Chapter 5

QUANTITATIVE COMPUTATIONAL METHODS

5.1 Determination of MW and MWD from Storgae Modulus G'

5.1.1 The Governing Equation

The dynamic storage modulus in the terminal and plateau zones contain a complete spectrum of molecular relaxation times. The deconvolution of G' data in those zones, therefore, can be employed to obtain the molecular weight distribution curve.

Based on Doi-Edwards reputation theory [7], the linear viscoelastic storage modulus for a polydisperse polymer can be expressed as [6]

$$G'(\omega) \int_{-\infty}^{\infty} D(\tau) \frac{8}{\pi^2} Gn^0 \sum_{\text{odd } p} \left(\frac{1}{p^2}\right) \frac{(\omega\tau/p^2)^2}{1 + (\omega\tau/p^2)^2} \, d \ln \tau \qquad (5.1)$$

where $G(\omega)$ is the dynamic storage modulus at angular frequency, τ the relaxation time for a monodisperse species of molecular weight M in the polydisperse blend, Gn^o the well defined plateau modulus, $D(\tau)$ the weight-fraction differential molecular weight distribution function in τ scale, and p the odd integers.

The molecular weight distribution function $D(\tau)$ can be obtained by inverting the integral in Eq. (5.1), using the $G'(\omega)$ data in terminal and plateau zones.

5.1.2 The Approximation of $G'(\omega)$

The first step of calculation is to approximate the $G'(\omega)$ data by a continuous function. Wu [6] assumed that the experimental G' data in the terminal zone could be expressed by

$$G'(\omega) = \sum_j \frac{G_j^o (\omega \tau_j)^{c_j}}{1 + (\omega \tau_j)^{c_j}} \tag{5.2}$$

with the constraint, $Gn^o = \sum_j G_j^o$.

In Eq. (5.2) G_j^o, τ_j and c_j are the numerical constants to be obtained by nonlinear curve fitting. For the convenience of calculation, let $x = \log \omega$ and substitute this into Eq. (5.2) to find

$$G'(\log \omega) = \sum_j \frac{G_j^o (\log \omega \tau_j)^{c_j}}{1 + (\log \omega \tau_j)^{c_j}}$$

$$= \sum_j \frac{G_j^o \tau_j^{c_j} 10^{\log \omega c_j}}{1 + \tau_j^{c_j} 10^{\log \omega c_j}}$$

or

$$G'(x) = \sum_j \frac{G_j^o \tau_j^{c_j} 10^{c_j x}}{1 + \tau_j^{c_j} 10^{c_j x}} \tag{5.3a}$$

Upon letting $A_j = G_j^o$, $B = \tau_j$, Eq. (5.3a) can be rewritten as

$$G'(x) = \sum_j \frac{A_j B_j^{c_j} 10^{c_j x}}{1 + B_j^{c_j} 10^{c_j x}} \tag{5.3b}$$

and then normalized to $(G'/Gn^0)\times 100$. Equation (5.3b) was found to represent experimental $G'(\omega)$ data curve very satisfactory.

5.1.3 The Weight-Fraction MWD Function $D(\tau)$

The second step of calculation is to invert the integral in Eq. (5.1) to obtain $D(\tau)$. As Wu [6] pointed out that since the Kernel series in Eq. (5.1) converges rapidly, due to the existence of p term, it is reasonable to truncate the series to retain only the first term. The simplified form of Eq. (5.1) becomes

$$G'(\omega) = \int_{-\infty}^{\infty} D(\tau) \frac{8}{\pi^2} Gn^0 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \, d \ln \tau \qquad (5.4)$$

With this simplification, Eq. (5.1) can be derived from the phenomenological theory of linear viscoelasticity alone, and is independent of any molecular models.

Substituting Eq. (5.3b) into Eq. (5.4), and inverting the integral by Stieltje's transform [21], the weight-fraction differential MWD function $D(\tau)$ can be obtained as [6]

$$D(\tau) = \sum_j \left. \frac{(2A_j/\pi)\,(1/B_j)\,(10)^{c_j x} \sin(\pi c_j/2)}{(1/B_j)\,(10)^{2c_j x} + (2/B_j)\, 10^{c_j x} \cos(\pi c_j/2) + 1} \right|_{\tau = 1/\omega} \qquad (5.5)$$

where B_j, C_j are obtained from $(G'/Gn^0)\times 100$ curve fitting.

5.1.4 Convert $D(\tau)$ from τ Scale to M Scale

To convert $D(\tau)$ from τ scale to the relative molecular weight M scale, the following relation was used [6]

$$\tau = \lambda M^{\beta} \qquad (5.6)$$

where λ and β are constants for the given polymer. τ is the longest relaxation time, which is approximately equal to β from $(G'/G_n^o)\times 100$ curve fitting. This relation comes from the assumption that the molecular weight of a given polymer can be represented by a single relaxation time. This equation will convert $D(\tau)$ from τ scale to relative molecular weight Mr scale as D(M).

5.1.5 The Scaling Factor S

The last step in calculation is to convert the D(M) from relative molecular weight Mr scale to absolute weight average molecular weight scale Mw. The scaling factor is defined as [6]

$$S = Mw/Mr \tag{5.7}$$

or

$$\log S = \log Mw - \log Mr \tag{5.8}$$

Here S is the scaling factor which is obtained by iteration method. The absolute weight average molecular weight Mw measured by GPC is used as the calibration point for iterations. The weight-fraction molecular weight distribution function is then normalized to

$$\int_{-\infty}^{\infty} D(\log M)\, d(\log M) = 100 \tag{5.9}$$

The various average molecular weights are obtained by

$$Mn = \int_{-\infty}^{\infty} D(\log M)\, d(\log M) / \int_{-\infty}^{\infty} [D(\log M)/M]\, d(\log M) \tag{5.10}$$

$$Mw = \int_{-\infty}^{\infty} D(\log M)\, M\, d(\log M) / \int_{-\infty}^{\infty} D(\log M)\, d(\log M) \tag{5.11}$$

$$Mz = \int_{-\infty}^{\infty} D(\log M)\, M^2\, d(\log M) / \int_{-\infty}^{\infty} D(\log M)\, M\, d(\log M) \tag{5.12}$$

5.2 Determination of MW and MWD from Relaxation Modulus G(t)

5.2.1 The Governing Equation

The relaxation modulus spectrum of a polymer melt in the terminal and plateau zones contain a complete spectrum of molecular relaxation times, which, like dynamic modulus G', can also be deconvoluted to obtain the molecular weight distribution curve.

For a monodisperse polymer, the stress relaxation modulus is given by [9]

$$G(t) = \int_{-\infty}^{\infty} Gn^{o}\ H(\tau)\ \exp(-t/\tau)\ d\ \ln\tau \tag{5.13}$$

Where G(t) is the relaxation modulus at time t, Gn^{o} is the plateau modulus, $H(\tau)$ the relaxation time spectrum, τ the longest relaxation time of a monodisperse of molecular weight M in polydisperse blend. The relaxation time spectrum $H(\tau)$ is associated with the volume-fraction differential molecular weight distribution function P(M).

The relaxation time spectrum at $\tau = t$ is obtainable in first approximation as the negative slope of the relaxation modulus

$$H(\tau) = - \left.\frac{d\ G(t)}{d\ \ln t}\right|_{t\ =\ \tau} \tag{5.14}$$

5.2.2 The Approximation of G(t)

The first step of calculation is to find a continuous function to represent the step responses of G(t). Since both G(t) and $G'(\omega)$ are a measure of stored elastic energy, and a dynamic measurement at frequency ω is qualitatively equivalent to a transient one at $t = 1/\omega$, their graphs are found approximately mirror image to each other reflected in

the modulus axis [11]. Based on Wu's empirical equation for G'(ω) given in [6], Eq. (5.1), G(t) can be expressed as [9]

$$G(t) = \sum_j \frac{G_j^o \, \tau_j^{\alpha_j} (1/t)^{\alpha_j}}{1 + (\tau_j)^{\alpha_j} \; (1/t)^{\alpha_j}} \tag{5.15}$$

with $t = 1/\omega$, and the constraint, $Gn^o = \sum_j G_j^o$. The quantities G_j^o, τ_j and α_j are constants defined by nonlinear curve fitting. Upon letting x = log t, Eq. (5.13) becomes

$$G(\log t) = \sum_j \frac{G_j^o \, \tau_j^{\alpha_j} (1/\log t)^{\alpha_j}}{1 + (\tau_j)^{\alpha_j} \; (1/\log t)^{\alpha_j}}$$

$$= \sum_j \frac{G_j^o \, \tau_j^{\alpha_j} \, e^{-2.303\alpha_j \log t}}{1 + \tau_j^{\alpha_j} \, e^{-2.303\alpha_j \log t}}$$

$$= \sum_j \frac{G_j^o}{(1/\tau_j)^{\alpha_j} \, e^{2.303\alpha_j \log t} + 1}$$

or

$$G(x) = \sum_j \frac{G_j^o}{(1/\tau_j)^{\alpha_j} \, e^{2.303\alpha_j x} + 1} \tag{5.16}$$

By letting $B_j = (1/\tau_j)^{\alpha_j}$, $C = 2.303\alpha_j$, and j = 1, Eq. (5.16) can be rewritten as

$$G(x) = \frac{G_n^o}{B \, e^{cx} + 1} \tag{5.17}$$

Thus, an approximation function of G(t) for a given polymer could be obtained by nonlinear curve fitting with the given G(t) data.

5.2.3 The Volume-Fraction Differential MWD Function

The volume-fraction differential molecular weight distribution function is given by [9]

$$P(M) = \frac{1/\sqrt{2}\ H(M)}{[\int_{\ln M}^{\infty} H(M)\ d\ \ln M]^{1/2}}$$

or

$$P(M) = \frac{1/\sqrt{2}\ H(M)}{2.303\ [\int_{2.303\ \log M}^{\infty} H(M)\ \log M]^{1/2}} \tag{5.18}$$

For the convenience of calculation, define

$$R(t) = 1 - G(t)/Gn^{0} \tag{5.19}$$

Substituting Eq. (5.17) into Eq. (5.19), with x = log t, yields

$$R(x) = 1 - \frac{1}{B\ e^{cx} + 1}$$

$$= \frac{B\ e^{cx}}{B\ e^{cx} + 1} \tag{5.20}$$

Substituting Eq. (5.20) into Eq. (5.14), the relaxation time spectrum is approximated to

$$H(x) = [dR(x)/dx]_{x=\log t} \tag{5.21}$$

By differentiating Eq. (5.20) with respect to the limit log t, we obtain

$$H(x) = dR(x)/dx$$

$$= \frac{B\ C\ e^{cx}\ (B\ e^{cx} + 1) - B\ C\ e^{cx}\ B\ e^{cx}}{(B\ e^{cx} + 1)^2}$$

$$= \frac{B\ C\ e^{cx}\ (B\ e^{cx} + 1 - B\ e^{cx})}{(B\ e^{cx} + 1)^2}$$

$$= \frac{B\ C\ e^{cx}}{(B\ e^{cx} + 1)^2} \tag{5.22}$$

Thus, the volume-fraction differential MWD function P(M) can be calculated through a combination of Eqs. (5.18) and (5.22).

5.2.4 Convert P(M) from τ Scale to M Scale

To convert $H(\tau)$ from τ scale into M scale, the following relation was used

$$\tau = \lambda\ M^{\beta} \tag{5.23}$$

where τ is the τ_j in Eq. (5.17) and M is the absolute weight average molecular weight Mw measured by light scattering method.

5.2.5 The Scaling Factor S

Finally, the relative molecular weight Mr scale is converted to the absolute weight average molecular weight scale Mw by using the scaling factor

$$S = Mw/Mr \tag{5.24}$$

or

$$\log s = \log Mw - \log Mr \tag{5.25}$$

The same iteration method is used here to obtain S as discussed before.

The volume-fraction molecular weight distribution function is normalized to

$$\int_{-\infty}^{\infty} P(M)\ d \log M = 100 \qquad (5.26)$$

Chapter 6

RESULTS AND DISCUSSION

6.1 Material

The material used in this study is poly(arylene ether ketone) polymers (PAE). This high performance thermoplastic material was chosen because of its potential use as structural resins in aerospace vehicles. The molecular weight of such polymers range from 9,600 to 113,000 g/mole as measured by light scattering. All samples used in this study had molecular weights above the critical entanglement value Mc.

The poly(arylene ether ketone) polymers were synthesized from the nucleophilic aromatic substitution reaction of 1,3-bis (4-fluorobenzoyl) benzene with 2,2-bis (4-hydroxyphenyl) propane as shown in Fig. 6.1, using N,N-dimethylacetamide (DMAc) solvent with 2% solids content (ω/v) and a slight excess of powdered potassium carbonate. Toluene was used to azeotrope the water formed and the reaction was stirred at 155°C overnight under a nitrogen atmosphere.

The physical properties of poly(arylene ether ketones) have been characterized by Jensen and Hergenrother [22] and are listed in Table 6.1.

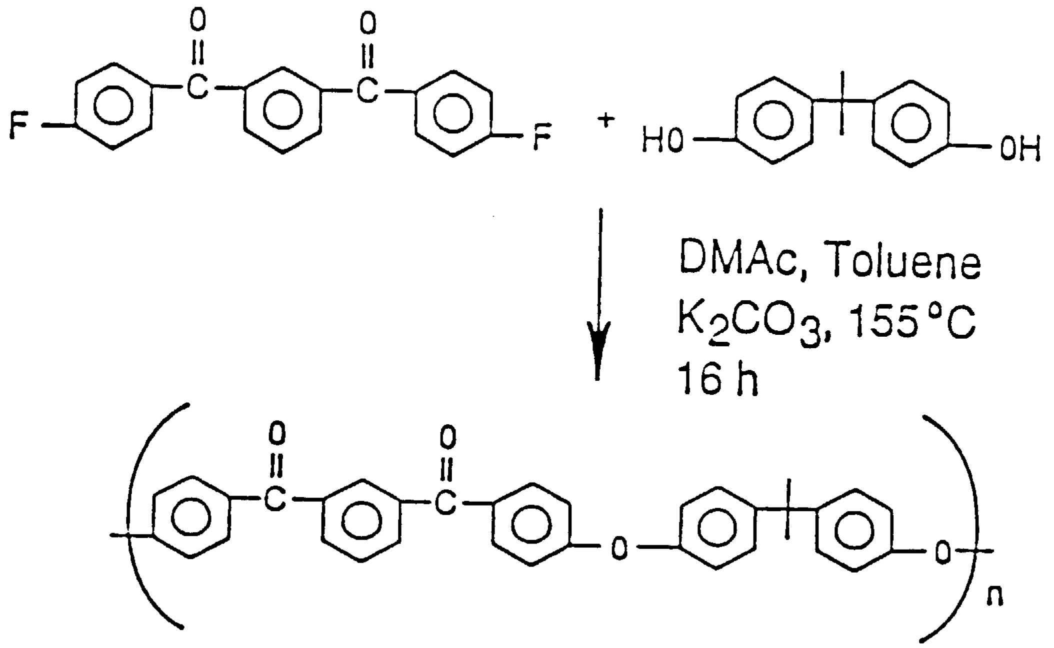


Fig. 6.1 Synthesis of poly (arylene ether ketone).

Table 6.1 Physical properties of poly(arylene ether ketones) [23].

Sample	r^1	η_{inh} (dL/g)^2	Tg (°C)^3
I	0.84	0.21	138
II	0.88	0.26	143
III	0.90	0.30	145
IV	0.94	0.40	159
V	0.95	0.55	152
VI	0.98	0.87	156

1. monomer ratio (BPA: 1,3-FBB)
2. measured in 0.5% solids in $CHCl_3$ at 25°C
3. measured by DSC at 20°C/min heating rate

6.2 Experimental Results

6.2.1 Measurements of Linear Viscoelastic Properties of PAE

The six polymers are designated hereinafter from I to VI in the order of increasing molecular weight. The dynamic modulus data G' and G" for all poly(arylene ether ketone) samples were measured under isothermal condition over a temperature range of 160°C to 280°C. Typical results of G' and G" data, measured at various temperatures, are shown in Fig. 6.2 for sample IV which has a weight average molecular weight Mw of 31,400 g/mole. The time-temperature superposition principle was employed here to reduce the G' and G" curves at different temperatures to a single master curve at the reference temperature of 200°C. The shift factor was calculated by WLF form [11] as

$$\log a_T = \frac{- C_1(T - T_c)}{(C_2 + T - T_c)} \tag{6.1}$$

where C_1 and C_2 are two material constants, T is the measured temperture in °C, and T_c is the reference temperature. Table 6.2 lists C_1, C_2 and a_T for all PAE samples. The dynamic moduli G' and G" master curves for all PAE samples are displayed in Figs. 6.3 and 6.4. The plateau modulus Gn^o is defined by the following integration method [11]

$$Gn^o = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega)\, d \ln \omega \tag{6.2}$$

For PAE samples, the plateau modulus obtained was $Gn^o = 2.3\text{x}10^7$ (dynes/cm^2) [18].

6.2.2 Calculation of G(t)

Since the linear viscoelastic phenomena are all interrelated, it is possible to calculate any one of the viscoelastic functions from the

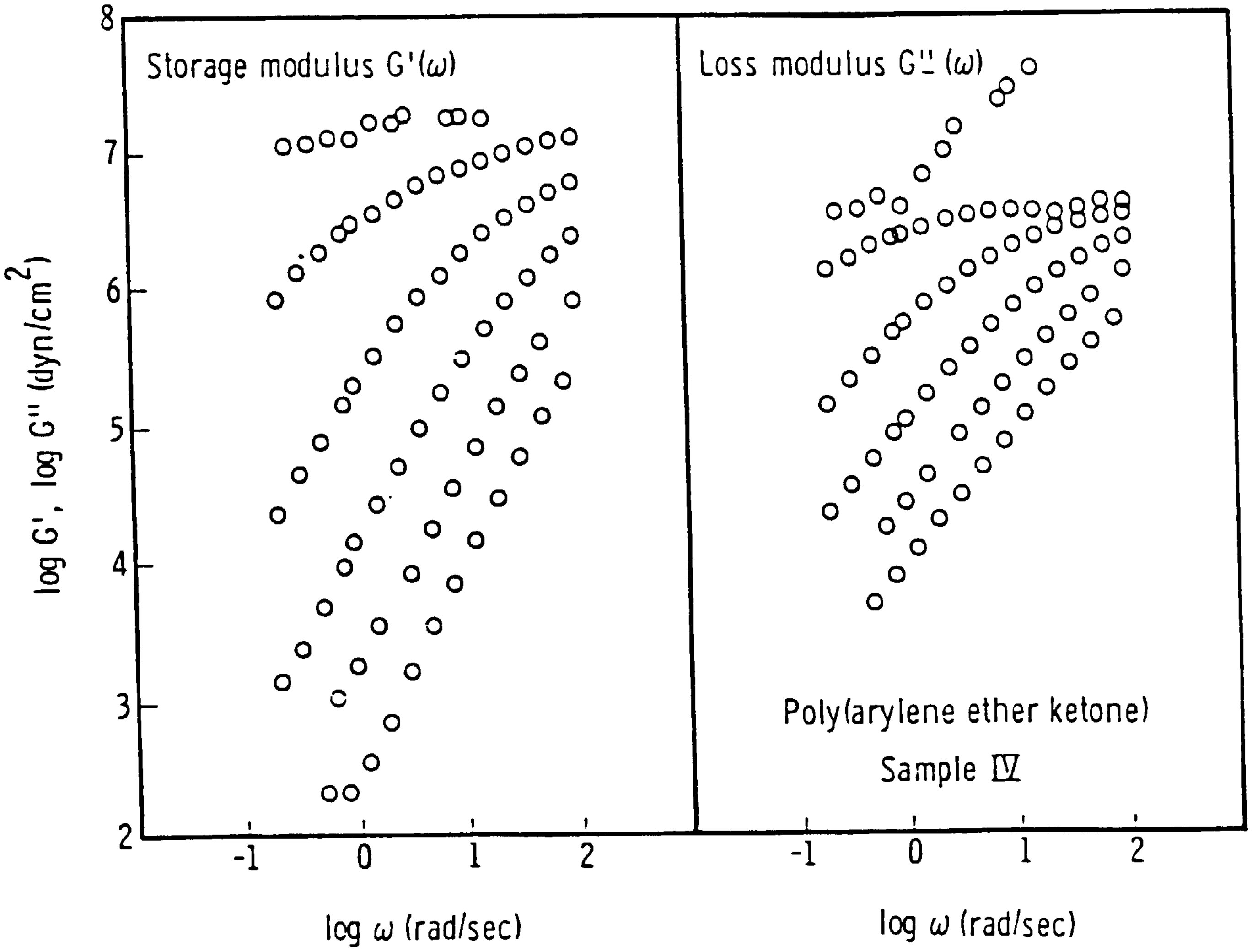


Fig. 6.2 Storage and loss moduli G'(ω) and G'' (ω) measured for sample IV at six temperatures. Starting with the data set at the top of the figure, the measurement temperature is 160, 180, 200, 220, 240 and 260°C respectively.

Table 6.2 Shift factors a_T for the poly(arylene ether ketone) samples

Sample T(°C)	I	II	III	IV	V	VI
150	14,680	---	---	---	---	---
160	567	1,420	1,420	3,924	15,500	---
170	61.6	100	---	---	366	---
180	11.4	14.2	14.1	18.8	30	30
190	2.9	---	---	---	---	---
200	1.0	1.0	1.0	1.0	1.0	1.0
220	---	0.17	0.17	0.145	0.11	0.11
240	---	---	0.047	0.036	0.020	0.025
260	---	---	---	0.013	0.008	---
270	---	---	---	---	---	0.004
280	---	---	---	---	0.0025	---
300	---	---	---	---	---	0.0008
C_1	4.26	4.53	4.65	4.87	5.275	5.275
C_2	101.56	97.92	99.91	95.35	91.04	91.04

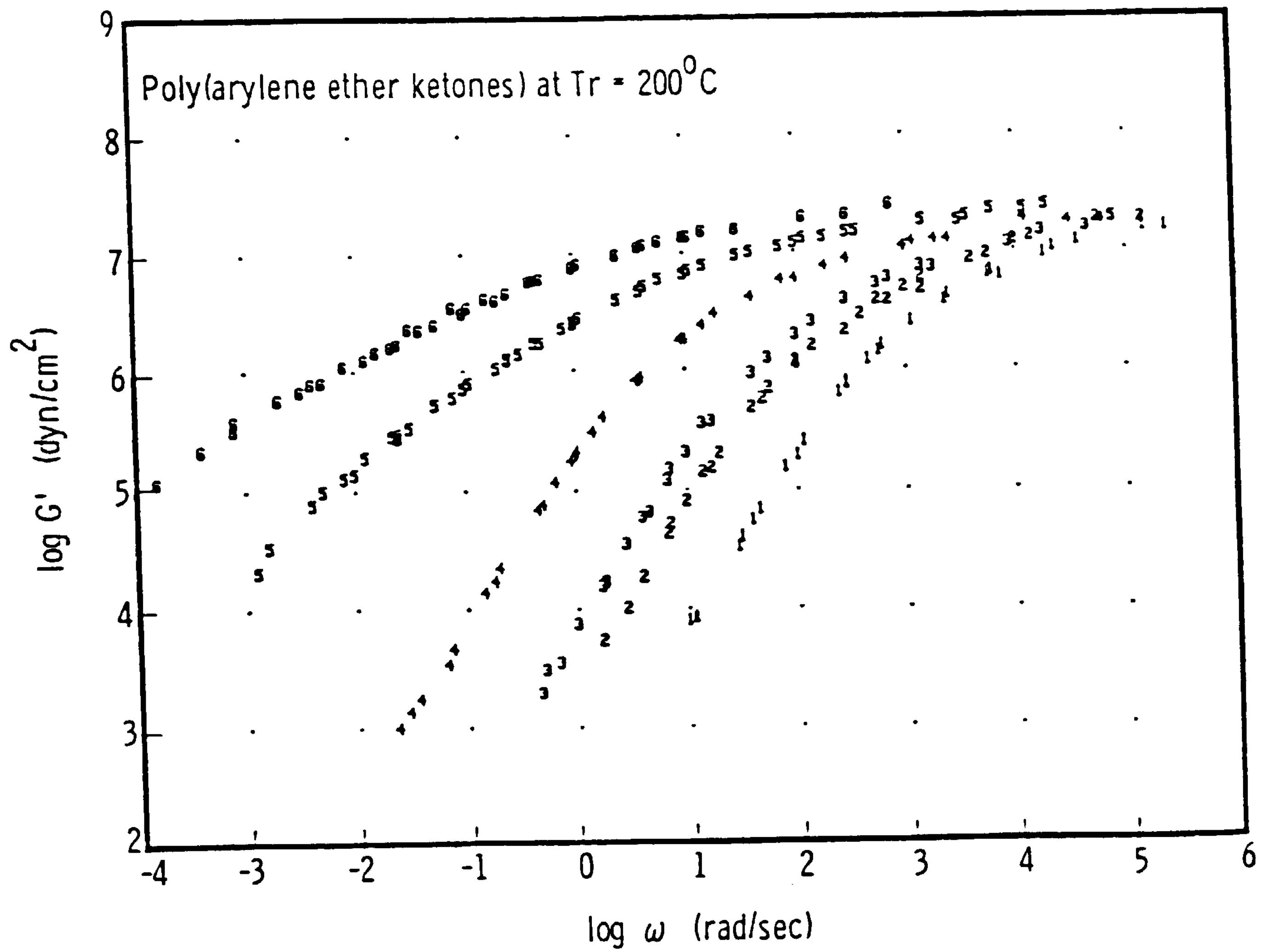


Fig. 6.3 Master curves at 200°C for the storage moduli G'(ω) of the six polymeric samples used in this study. The master curve for each sample is labelled by a numerical number from 1 to 6 which corresponds to sample I to VI.

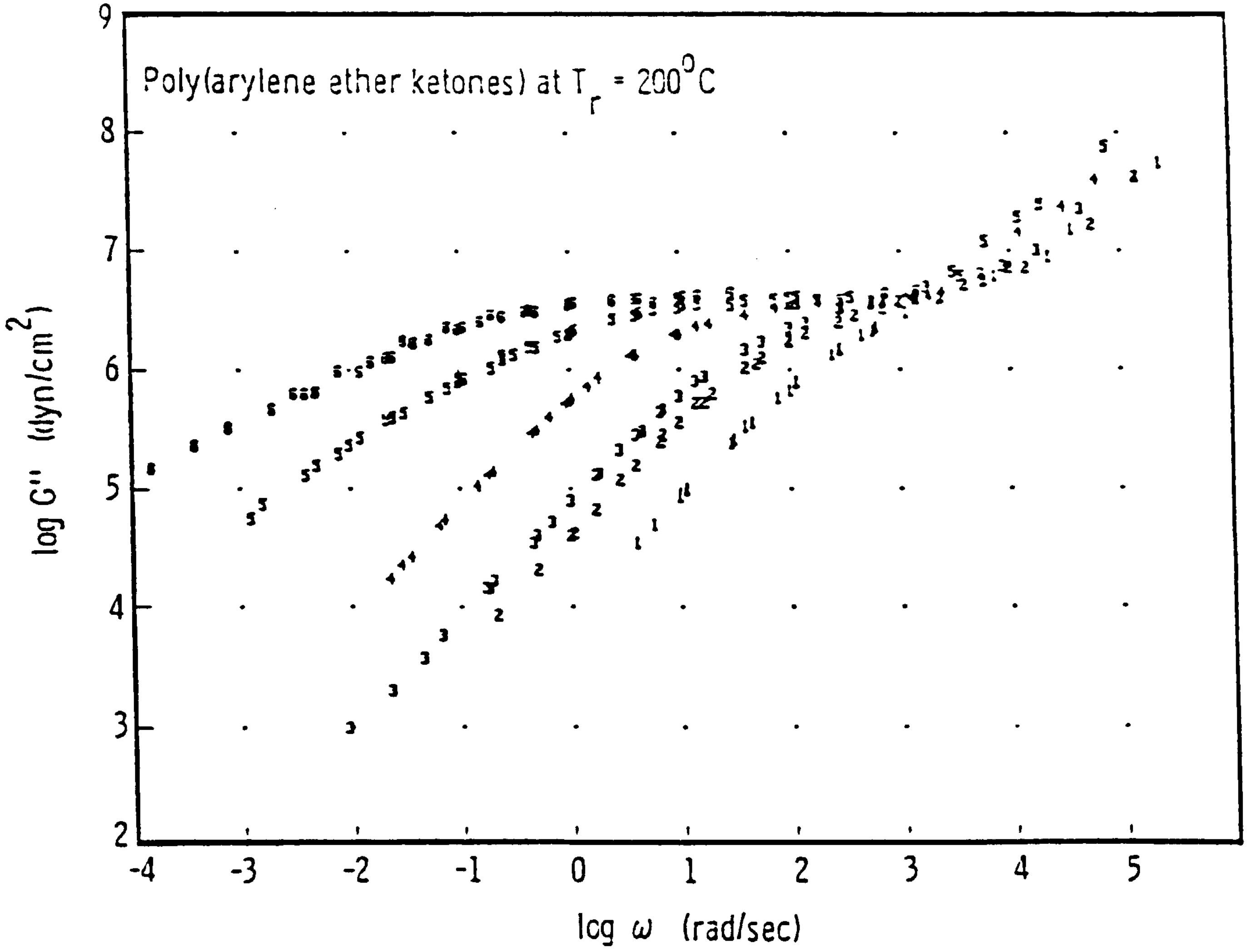


Fig. 6.4 Same as Fig. 6.3, except the master curves for the loss moduli G"(ω) are presented.

others that are directly measured. The equation for calculating G(t) from G' and G" used here is expressed as [11]

$$G(t) = G'(\omega) - 0.4G''(0.40\ \omega) + 0.014G''(10\ \omega) \qquad (6.3)$$

The results of calculated G(t) of all PAE samples are plotted in Fig. 6.5.

6.2.3 Results of Molecular Weight Measurements

The MW of poly(arylene ether ketone) samples are measured by light scattering and GPC methods. The light scattering (static/LALLs) method provided the absolute weight average molecular weight Mw of PAE samples. The gel permeation chromatography (GPC/LALLs) method provided the data of the weight average molecular weight Mw, the number average molecular weight Mn and the polydispersity ratio Mw/Mn. The results of these two methods are listed in Table 6.3.

6.3 Qualitative Methods in Determinations of MW and MWD

6.3.1 Method of Zeichner and Patel

Since G" is associated with the zero shear viscosity and G' is associated with the shear compliance Je^o, they are related to the molecular weight and the molecular weight distribution respectively. By shifting the G" and the G' master curves along the reduced frequency ω_R axis, Zeichner and Patel [1] had demonstrated that G' and G" curves for polymers with same MWD will superimpose one another.

Among the six PAE samples investigated here, samples I and II have same polydispersity ratio Mw/Mn of 2.1 to 2.2, and samples III and IV have polydispersity ratio of 1.5 to 1.6. The master curves of samples I

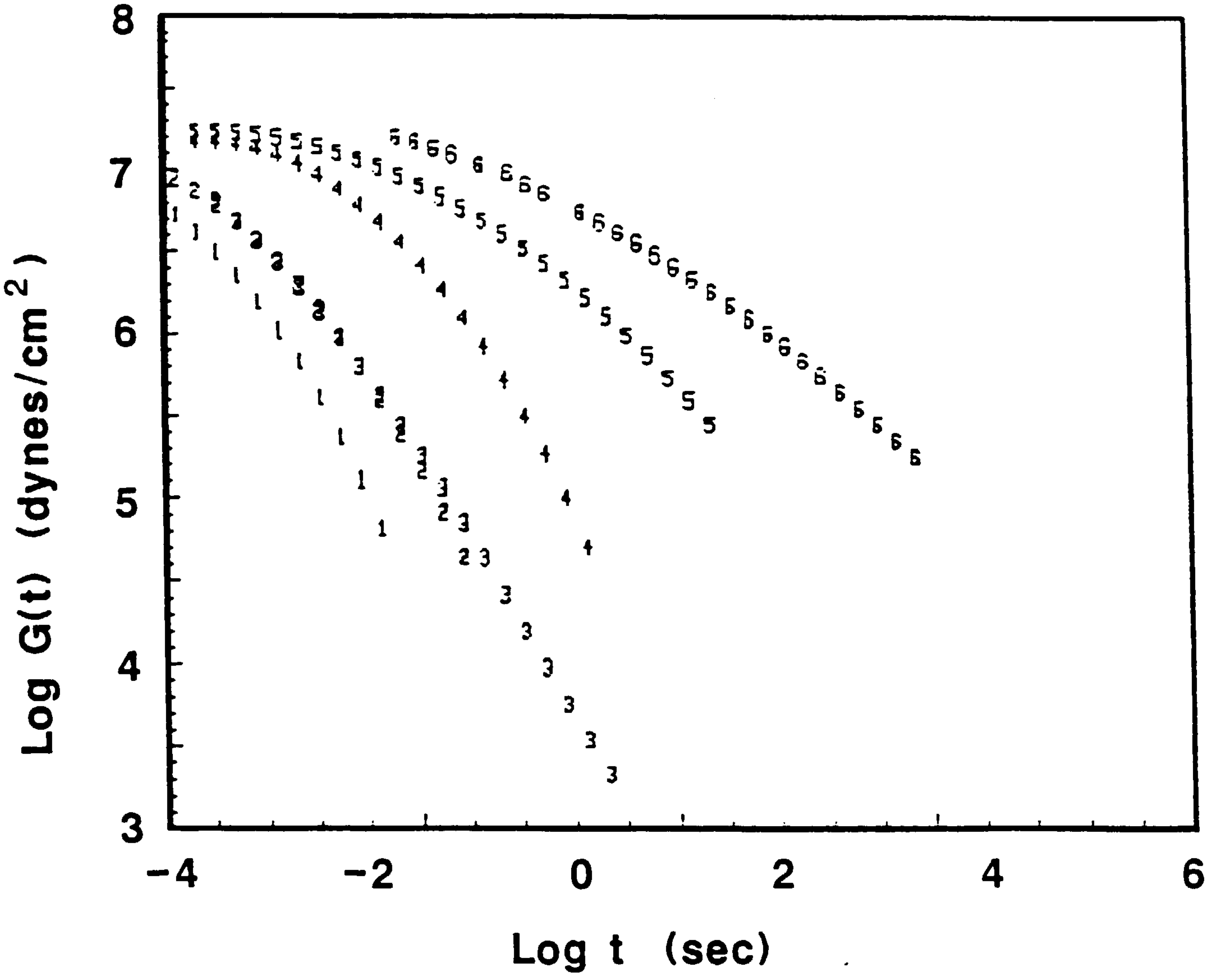


Fig. 6.5 Relaxation moduli G(t) calculated from G'(ω) and G"(ω) data of the six PAE samples. The G(t) curve for each sample is labelled by a numerical number from 1 to 6 which corresponds to sample I to VI.

Table 6.3 Molecular weights of six PAE samples measured by Light Scattering and GPC methods

Sample	Light Scattering	GPC/LALLs		
	Mw	Mw	Mn	Mw/Mn
I	9600	10000±200	4700±200	2.1±0.1
II	17100	13000±2000	6000±2000	2.2±0.5
III	18300	15500±400	10200±200	1.5±0.1
IV	31400	26300±300	16000±2000	1.6±0.2
V	59300	53000±1000	19000±300	2.75±0.02
VI	113000	112000±2000	50000±1000	2.24±0.02

and II are replotted in Fig. 6.6 in accordance with the method suggested by Zeichner and Patel, with the reduced frequency of $\omega_R = \eta_0 \omega$, where $\eta_0 = 8.5\text{x}10^3$ poises and $\eta_0 = 4.0\text{x}10^4$ poises for samples I and II respectively. It could be seen from the figure that G' and G" for these two samples with same MWD are superimposed to each other. Similar curves replotted in reduced frequency scales for samples III and IV (with $\eta_0 = 8.5\text{x}10^4$ poises for sample III and $\eta_0 = 7.5\text{x}10^5$ poises for sample IV) are shown in Fig. 6.7. Here again, the behavior suggested by Zeichner and Patel holds true for these PAE polymers.

Zeichner and Patel [1] also suggested that when G" and G' were plotted with respect to the reduced frequency, ω_R, polymers with different MWD will exhibit different slopes in the terminal zones. Comparing Figs. 6.6 and 6.7, it is noted that they are essentially identical and can be superimposed as shown in Fig. 6.8, which is in contrast with the prediction of Zeichner and Patel. For the PAE polymers studied here, the polydispersity ratio ranges from 1.5 to 2.7, the pair to be compared is 1.5 to 1.6 and 2.1 to 2.2, which is not different significantly. Therefore, the difference of the slope of G' and G" curves is difficult to find.

6.3.2 Method of Dormier, Tong and Laggase

The relation between molecular weight ratio and the shift factor, a_m, defined by Dormier, Tong and Laggase [3] is

$$\frac{(Mw)_h}{(Mw)_1} = a_m^{1/3.4}$$

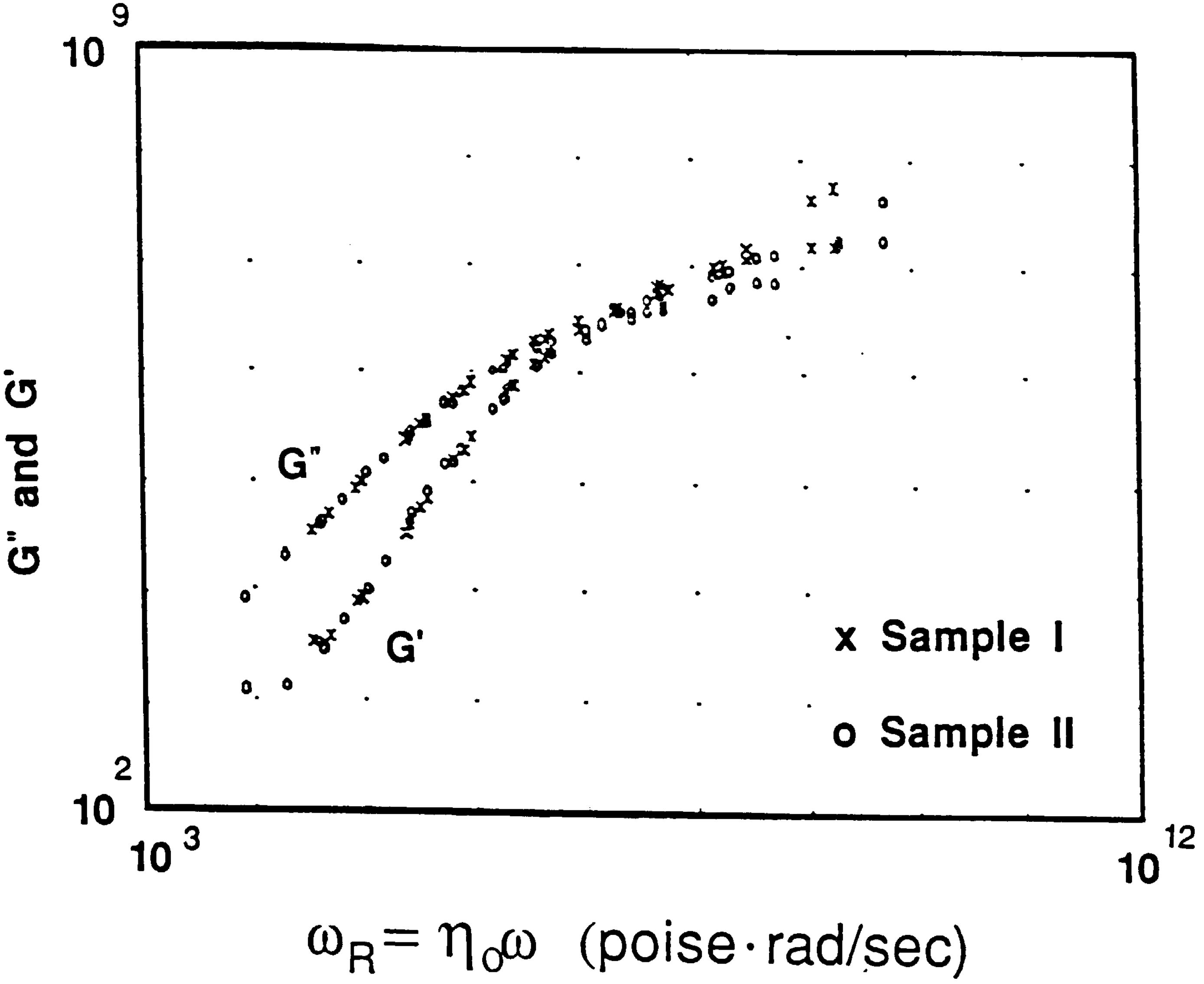


Fig. 6.6 Reduced master curves of dynamic moduli G' and G" for sample I and II with a polydispersity ratio of 2.1 to 2.2, and the zero shear viscosity $\eta_o = 8.5\times10^3$ poises and $\eta_o = 4.0\times10^4$ poises respectively.

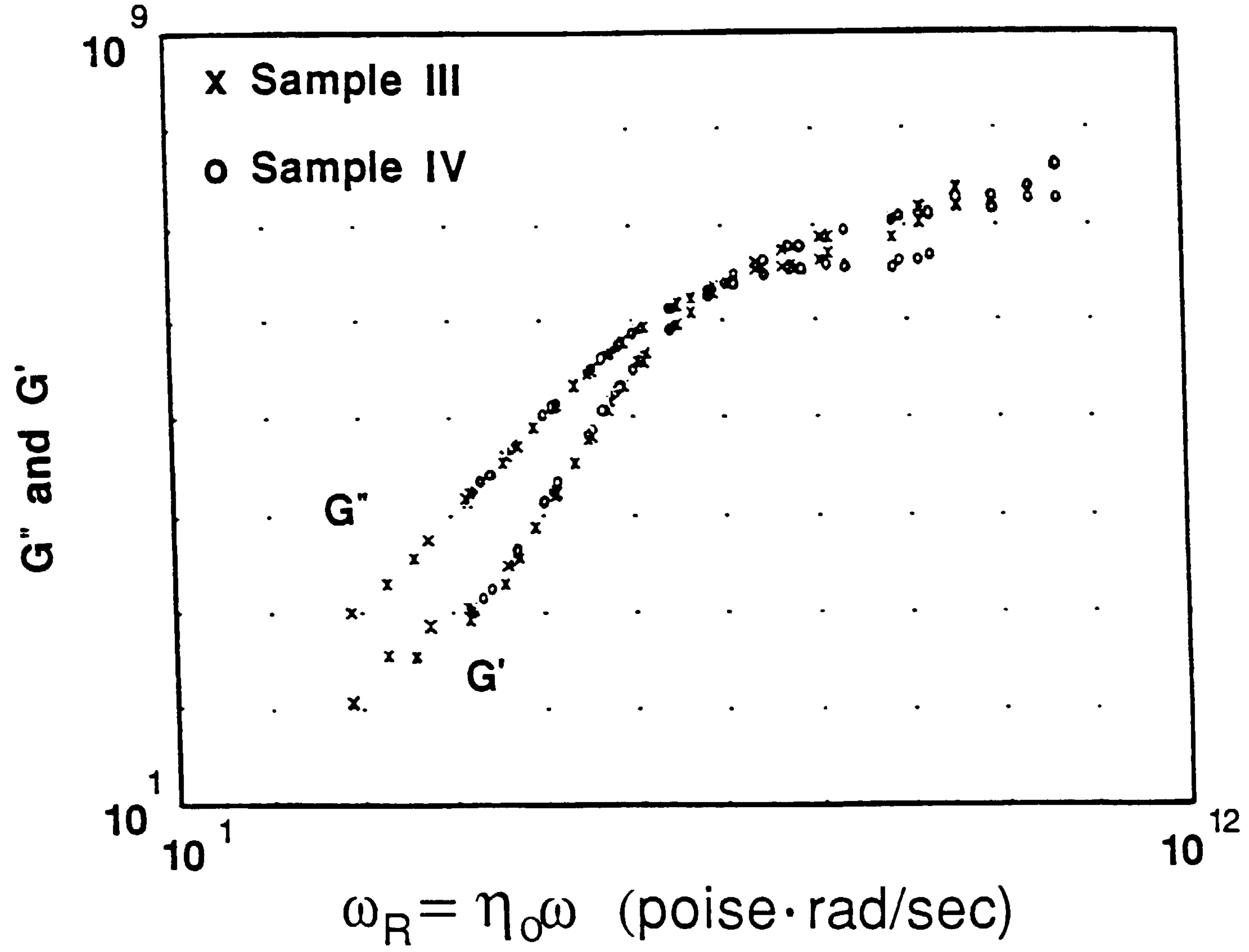


Fig. 6.7 Reduced master curves of dynamic moduli G' and G" for sample III and IV with a polydispersity ratio of 1.5 to 1.6, and the zero shear viscosity $\eta_0 = 8.5\times10^4$ poises and $\eta_0 = 7.5\times10^5$ respectively.

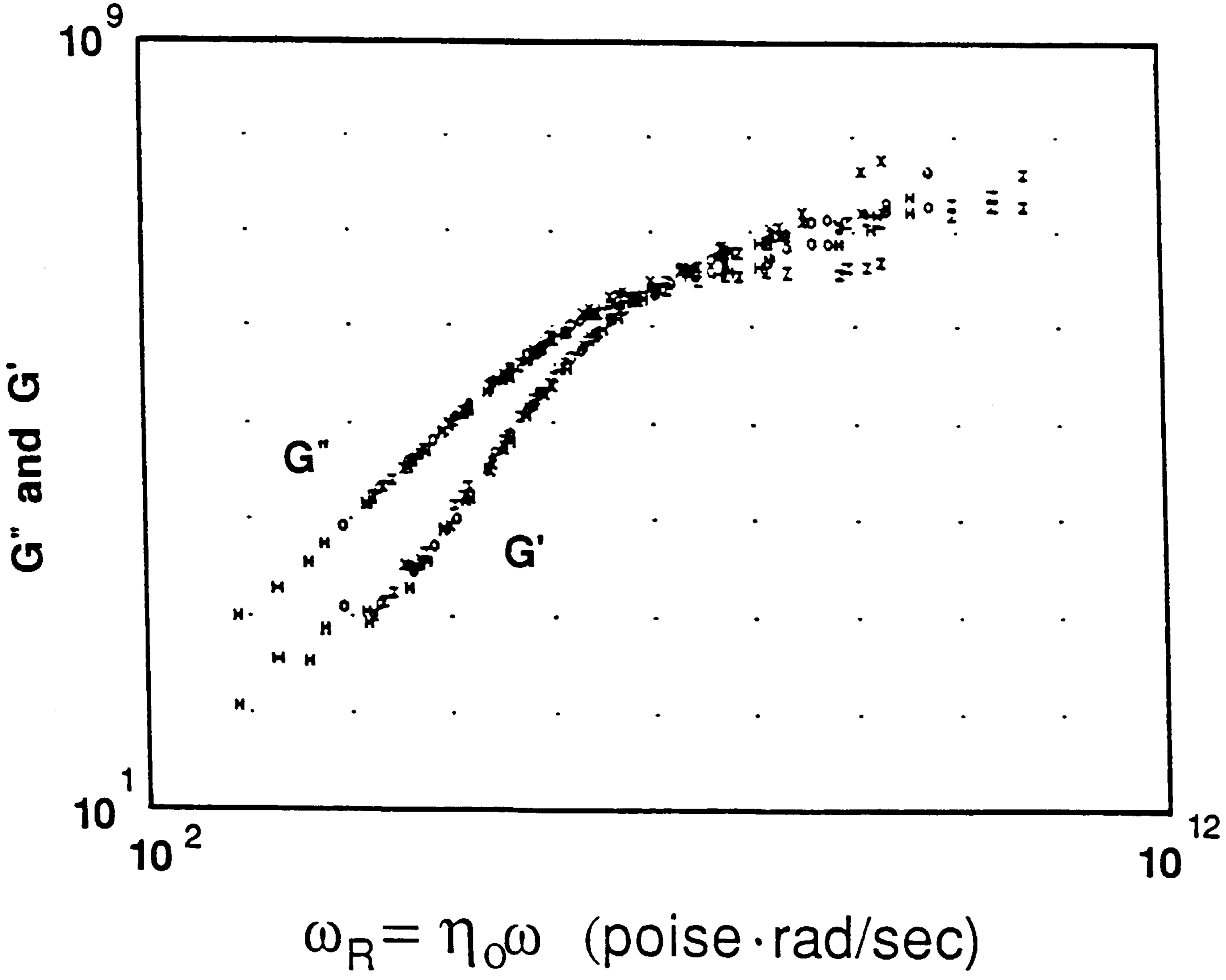


Fig. 6.8 The shifted form of reduced master curves of sample I, II, III and IV.

For poly(arylene ether ketones), the relation between η_o and Mw has been found as [17]

$$\eta_o \propto Mw^{5.126} \tag{6.4}$$

Thus, for PAE samples, the relation

$$(Mw)_h/(Mw)_1 = a_m^{1/5.126} \tag{6.5}$$

is used. Two different cases were considered and these are discussed below.

Case 1. Polymers with different MW and identical MWD

This is a comparison between two polymers that have different MW and same MWD. By shifting the G' and G" master curves of two polymers with different MW and identical MWD, the G' and G" curves will superimpose over a broad frequency range in the terminal zone. Since Je^o relates only on MWD for linear polymers of high molecular weight, and G' is associated with Je^o, thus, if two polymers have identical MWD, their G' curve should be superimposed. Master curves of dynamic moduli for samples I and II are shifted as shown in Fig. 6.9 because they both have Mw/Mn of 2.1 to 2.2 and different molecular weights. The master curves for sample III and IV are shifted in the same manner as shown in Fig. 6.10, with a polydispersity ratio Mw/Mn of 1.5 to 1.6 and different molecular weights. It can be seen that the G' and G" master curves of these two pairs of samples perfectly superimpose over a broad frequency range in the terminal zone. The shift factor, a_m, needed here to shift the higher Mw sample to obtain superposition are 4.38 and 9.43 respectively. The calculated Mr ratio presented in Table 6.4 shows agreement with the value obtained by GPC measurement.

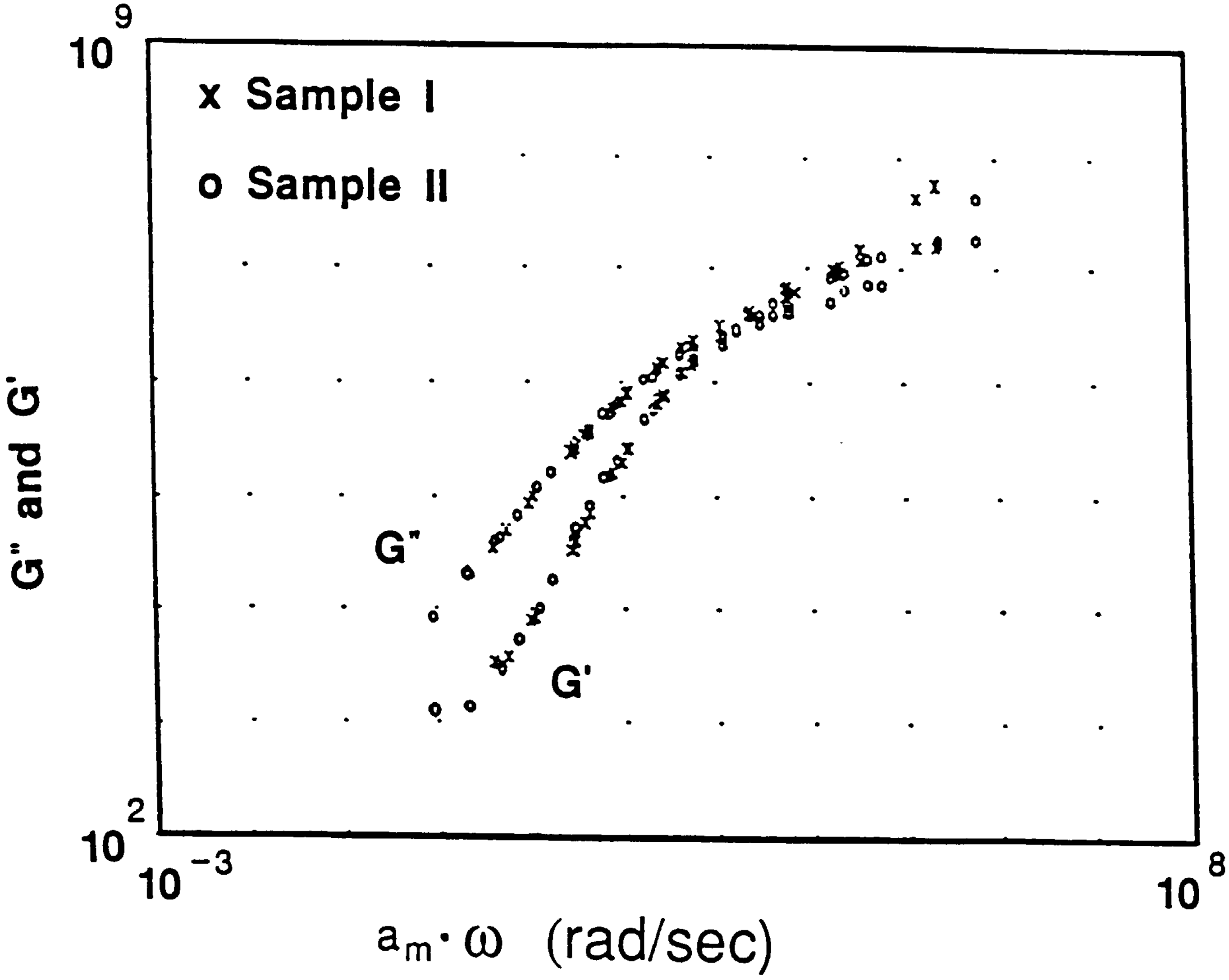


Fig. 6.9 Shifted form of G' and G" master curves of sample I and II with a shift factor a_m of 4.38.

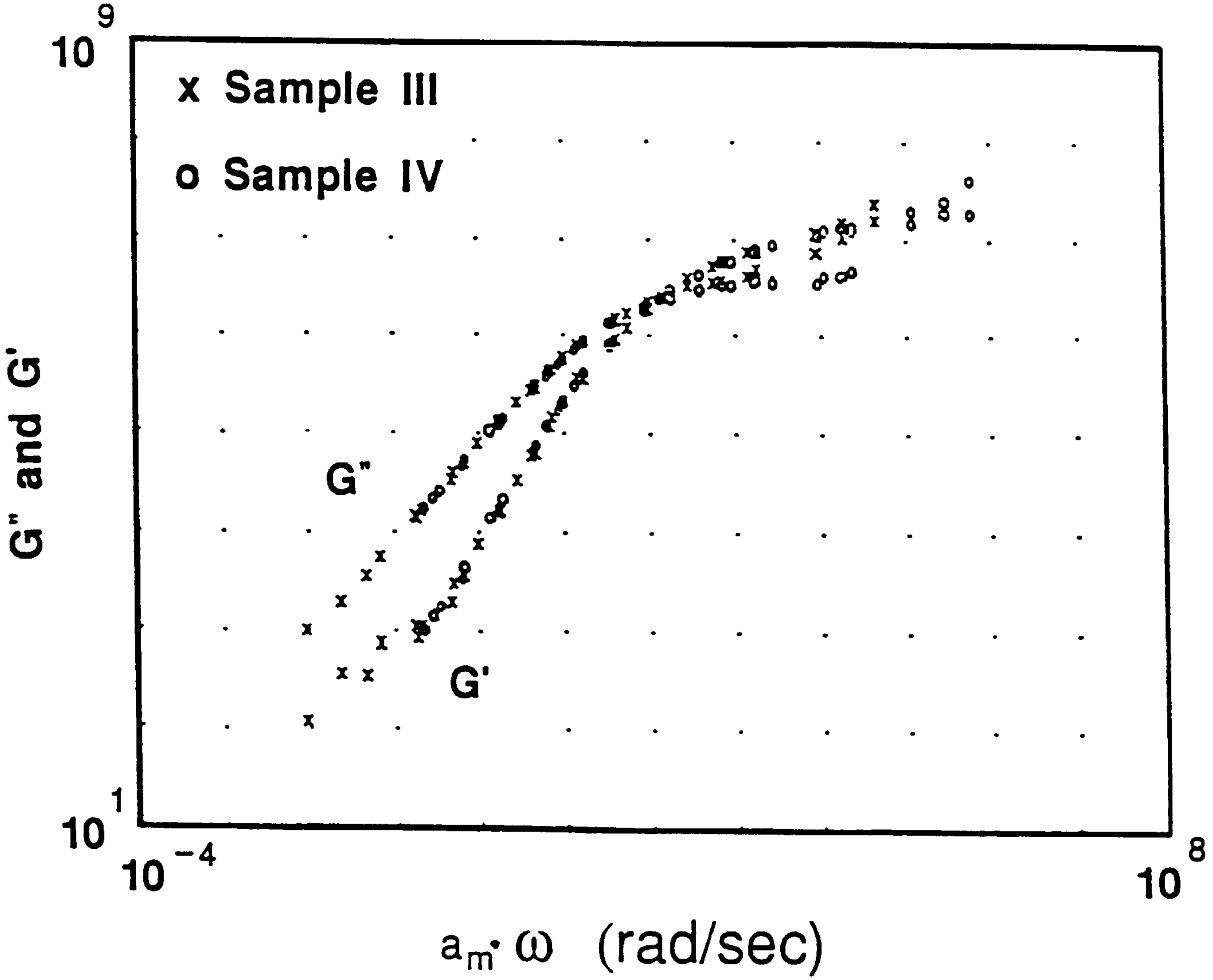


Fig. 6.10 Shifted form of G' and G" master curves of sample III and IV with a shift factor a_m of 9.43

Table 6.4 Molecular weight and molecular weight ratios of selected PAE samples measured by GPC and the method of Dormier, Tong and Lagasse [3]

Sample	GPC/LALLs			Rheology	
	Mw	Mw/Mn	$(Mw)_h/(Mw)_1$	a_m	$(Mw)_h/(Mw)_1$
I	10000	2.1	1.3	4.38	1.33
II	13000	2.2			
III	15500	1.5	1.697	9.43	1.549
IV	26300	1.6			
III	15500	1.5	2.968	256.2	2.95
V	53000	2.75			

Case 2. Polymers with different MW and different MWD

If two polymers have different MW and different MWD, the shift factor will be obtained by overlapping their G" curve at the low frequency limit. In this case, it is not possible to superimpose either G' or G" over a broad range of frequency due to differences in both molecular weight and molecular weight distribution. But different slopes of two master curves give qualitative information about the MWD.

Sample III and V have different MW and different MWD. The master curves of these two samples in their shifted form are presented in Fig. 6.11. In this case, it is impossible to superimpose the G' and G" data over a broad frequency range due to their different MW and MWD. The shift factor, a_m, needed here is 256.2, which is obtained by overlapping the G" data at the low frequency limit as shown in Fig. 6.11. The lower slope of G' at low frequency limit for sample V indicate that it has a broader MWD. Table 6.4 summarizes the calculated results of the ratio of their molecular weights and is compared with the value obtained by GPC method. Here, the agreement is obvious.

Examining the results in Table 6.4, it can be seen that the relation between the shift factor a_m and the Mw ratio is applied very well. This implies that the shift factor exactly corresponds to the zero shear viscosity η_0 for PAE polymers.

6.4 Quantitative Methods in Determination of MW and MWD

The quantitative method is to deconvolute the data of the storage modulus G' or the relaxation modulus G(t) in terminal and plateau zones to deterine the MW and MWD. The methods are discussed in Chap. 5, and the results are presented here.

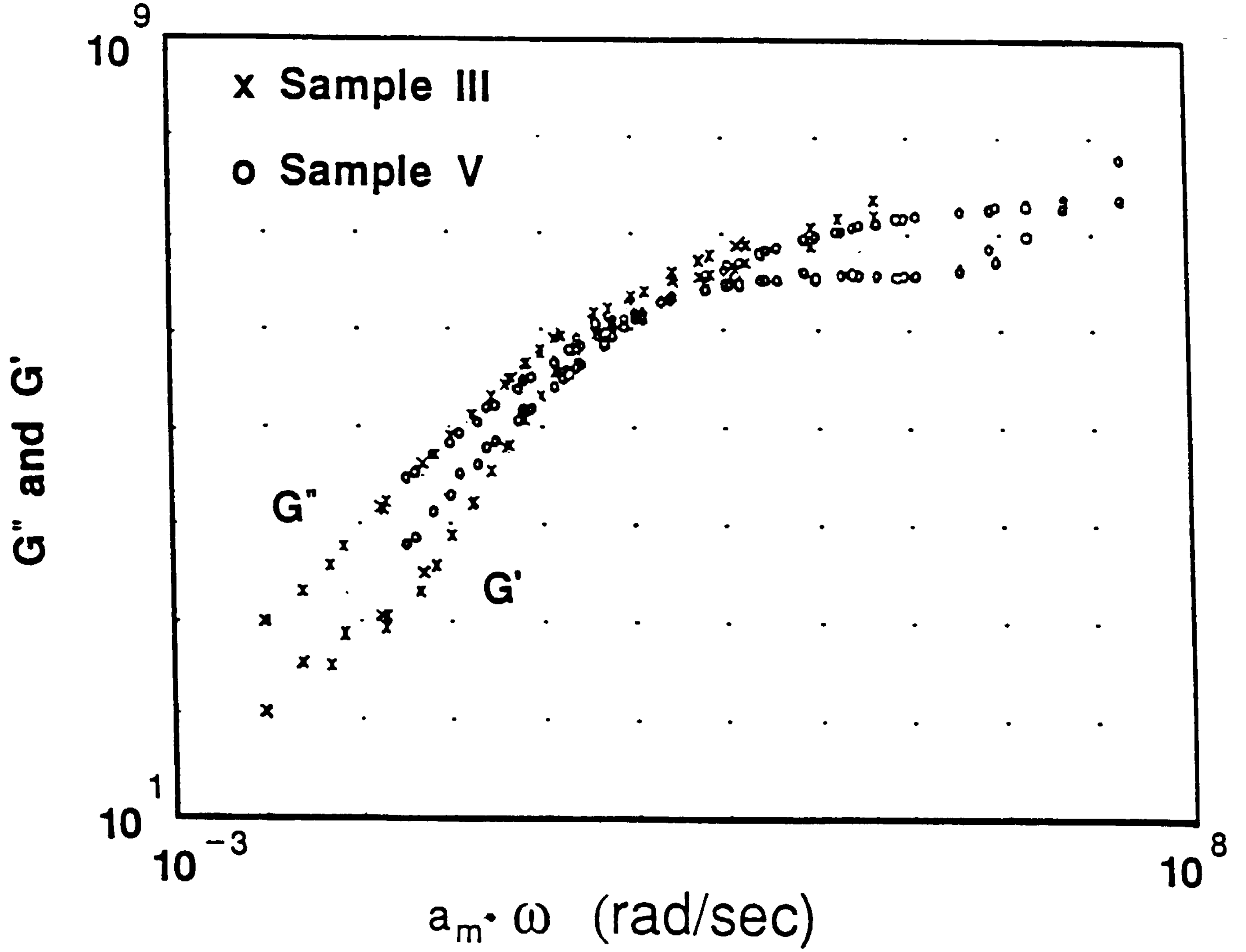


Fig. 6.11 Shifted form of G' and G" master curves of sample III and V with a shift factor a_m of 256.2

6.4.1 Deconvoluting the Storage Modulus G' to Determine the MW and MWD

6.4.1.1 The Approximation Function of G'. Table 6.5 lists the parameters of B and C for Eq. (5.3b), which is the approximated continuous function of G'. The values of B and C are determined by fitting the experimental G' data on $(G'/Gn^{0}) \times 100$ curve with $j = 1$ for all PAE samples. The Simplex nonlinear curve fitting algorithm is used for curve fitting. It can be seen that B is the parameter which is proportional to molecular weight as shown in Fig. 6.12. The higher the molecular weights, the greater the values of B. Comparison between the theoretical $(G'/Gn^{0}) \times 100$ curve and the experimental data for all six PAE samples is shown in Fig. 6.13. It is also noted that B is a parameter that positions the curve in the x direction. As the B value increases, the curve moves to the left. This is reasonable because B represents the relaxation time, which is associated with the molecular weight. Inspecting Fig. 6.13, it can be seen that the theoretical curve fits the experimental data in the terminal and plateau zones, and the data in the transition zone are isolated.

6.4.1.2 Conversion of the MWD Function D(τ) from τ Scale to M Scale. As discussed in Chap. 5, Eq. (5.6) is the relation to convert the MWD function $D(\tau)$ from τ scale to M scale. For PAE samples, the least squares regression gives $\lambda = -20.035$ and $\beta = 3.827$. Thus, we have

$$\log \tau = -20.035 + 3.827 \log M \qquad (6.6)$$

where M is the weight average molecular weight obtained from the light scattering measurement. Since $\tau = 1/\omega$, Eq. (6.6) can be rewritten as

Table 6.5 Values of B and C parameters of six PAE samples for Eq. (5.3b) determined from $(G'/G_n^0)\times100$ nonlinear curve fitting

Sample	B	C
I	0.000033	0.65
II	0.0001	0.60
III	0.000132	0.54
IV	0.0011	0.50
V	0.016	0.50
VI	0.29	0.50

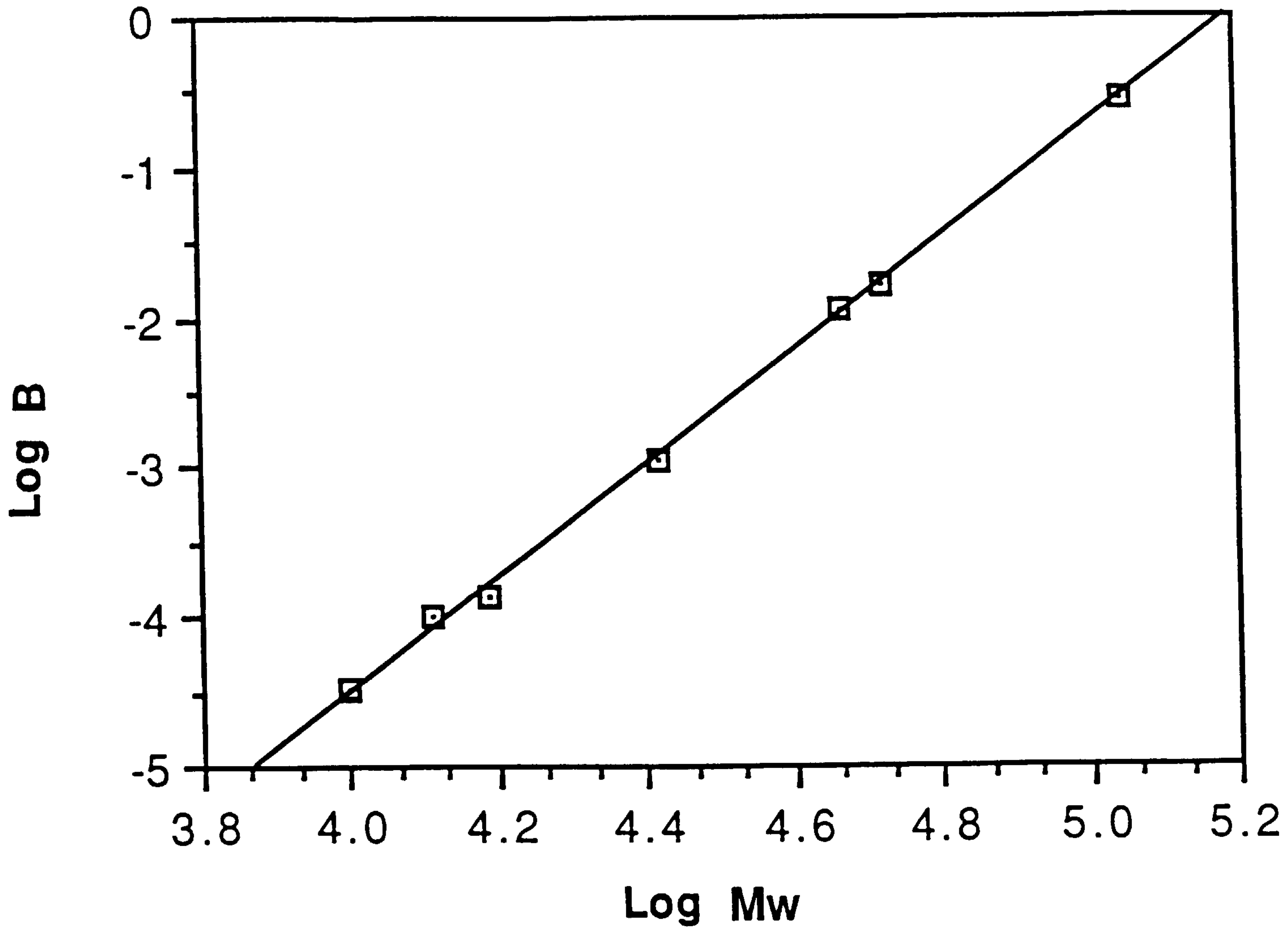


Fig. 6.12 Plot of parameter B vs. MW, with the MW is the weight average molecular weight obtained by GPC method

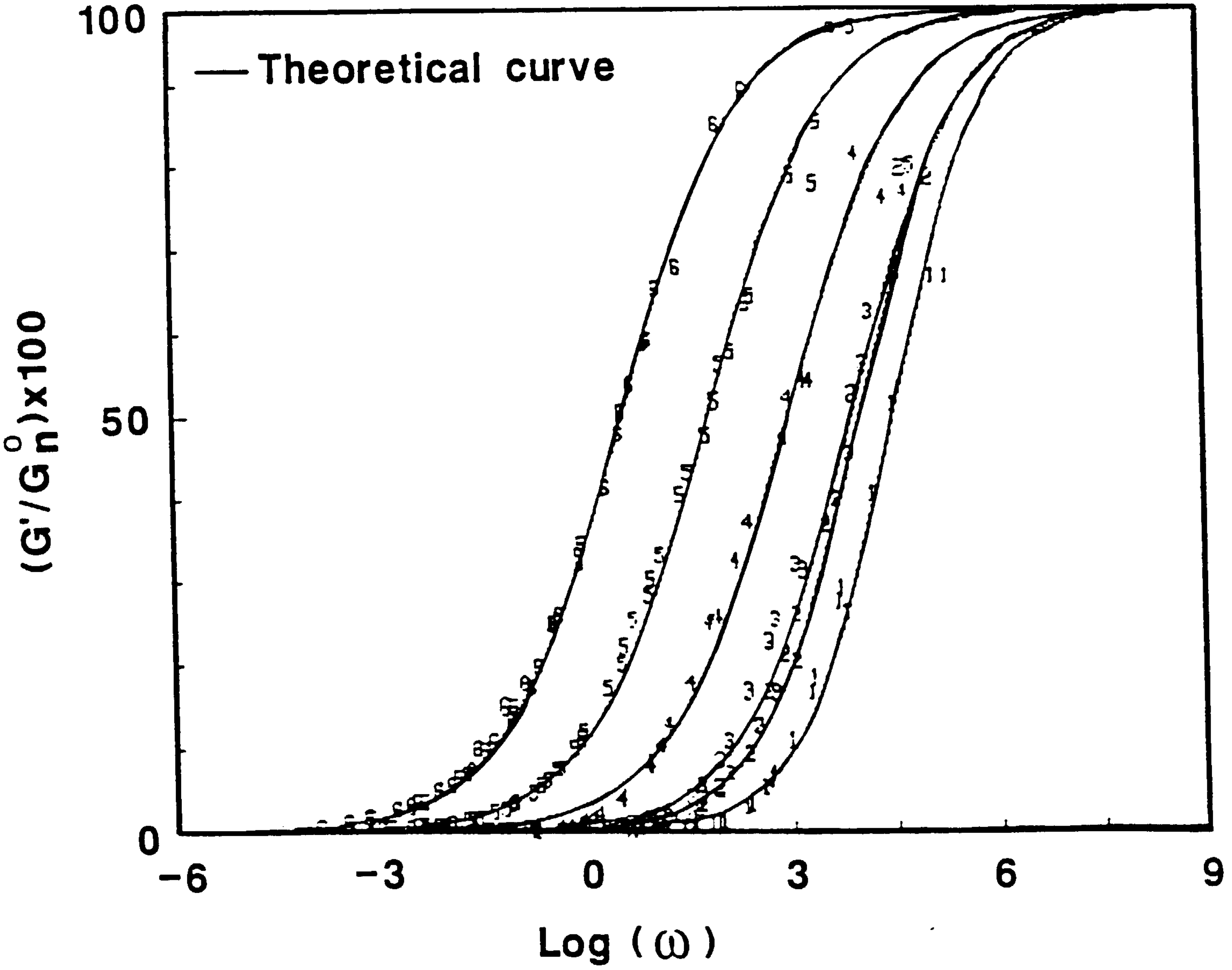


Fig. 6.13 Comparison between the theoretical (G'/Gn^o)x100 curve and the experimental G' data for six PAE samples. The experimental data for each sample are labelled by a numerical number from 1 to 6 which corresponds to sample I to VI

$$\log 1/\omega = -20.035 + 3.827 \log M \tag{6.7a}$$

or

$$\log \omega = -(-20.035 + 3.827 \log M) \tag{6.7b}$$

This equation gives the relation between ω and M, which is necessary since measured G' is a function of ω. With this relation, $D(\tau)$ can be inverted from $G'(\omega)$ and then converted to M scale.

6.4.1.3 <u>The Calculation of $D(\tau)$ and the Scaling Factor S</u>. The weight average molecular weight Mw and the number average molecular weight Mn are calculated by integrations of Eqs. (5.10) and (5.11). The MWD function $D(\tau)$ is calculated by Eq. (5.5) and then normalized according to Eq. (5.9). The scaling factor S, which is used to shift the MWD curve from the relative molecular weight Mr scale to the absolute weight average molecular weight Mw scale, is obtained by an iteration method. The Mw value obtained from GPC method is used as the calibration point in the iteration. An initial guess of S is given at the first iteration. If the Mw value obtained is not equal to the value of the calibration point, the S value is modified. The procedures are repeated again and again until the Mw value is equal to the value of the calibration point. The value of log S obtained ranged from 2 to 4.5.

The calculated values of Mw, Mn and Mw/Mn are compared with the value measured by light scattering and GPC methods and are listed in Table 6.6. A comparison of present results for Mw/Mn with that obtained by GPC, shows a rather poor agreement. The uncertainty in Mn value is up to 20% for samples III and IV. The calculated molecular weight distribution curves and the experimental data of all samples are compared in Fig. 6.14. Examining these results, it is noted that all PAE samples except sample I possess bimodal distributions in molecular

Table 6.6 Comparison of the molecular weights by Light Scattering, GPC and Rheological methods

Sample	Light Scattering	GPC/LALLS			G' (1)			G(t) (2)		
	Mw	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
I	9600	10000±200	4700±200	2.1±0.1	9957	5830	1.71	9949	7253	1.37
II	17100	13000±2000	6000±2000	2.2±0.5	12993	7008	1.85	13098	9160	1.43
III	18300	15500±400	10200±200	1.5±0.1	15630	7468	2.09	15631	11500	1.36
IV	31400	26300±300	16000±2000	1.6±0.2	26434	10734	2.46	26160	17394	1.50
V	59300	53000±1000	19000±300	2.75±0.02	53475	21749	2.46	52830	20332	2.60
VI	11300	112000±2000	50000±1000	2.24±0.02	111735	43621	2.56	111687	41320	2.70

(1) The molecular weight is determined by deconvoluting the G' data in terminal and plateau zones, with $\beta = 3.827$ and S is obtained by iteration method

(2) The molecular weights is determined by deconvoluting the G(t) data in terminal and plateau zones, with $\beta = 3.595$ and S is obtained by iteration method

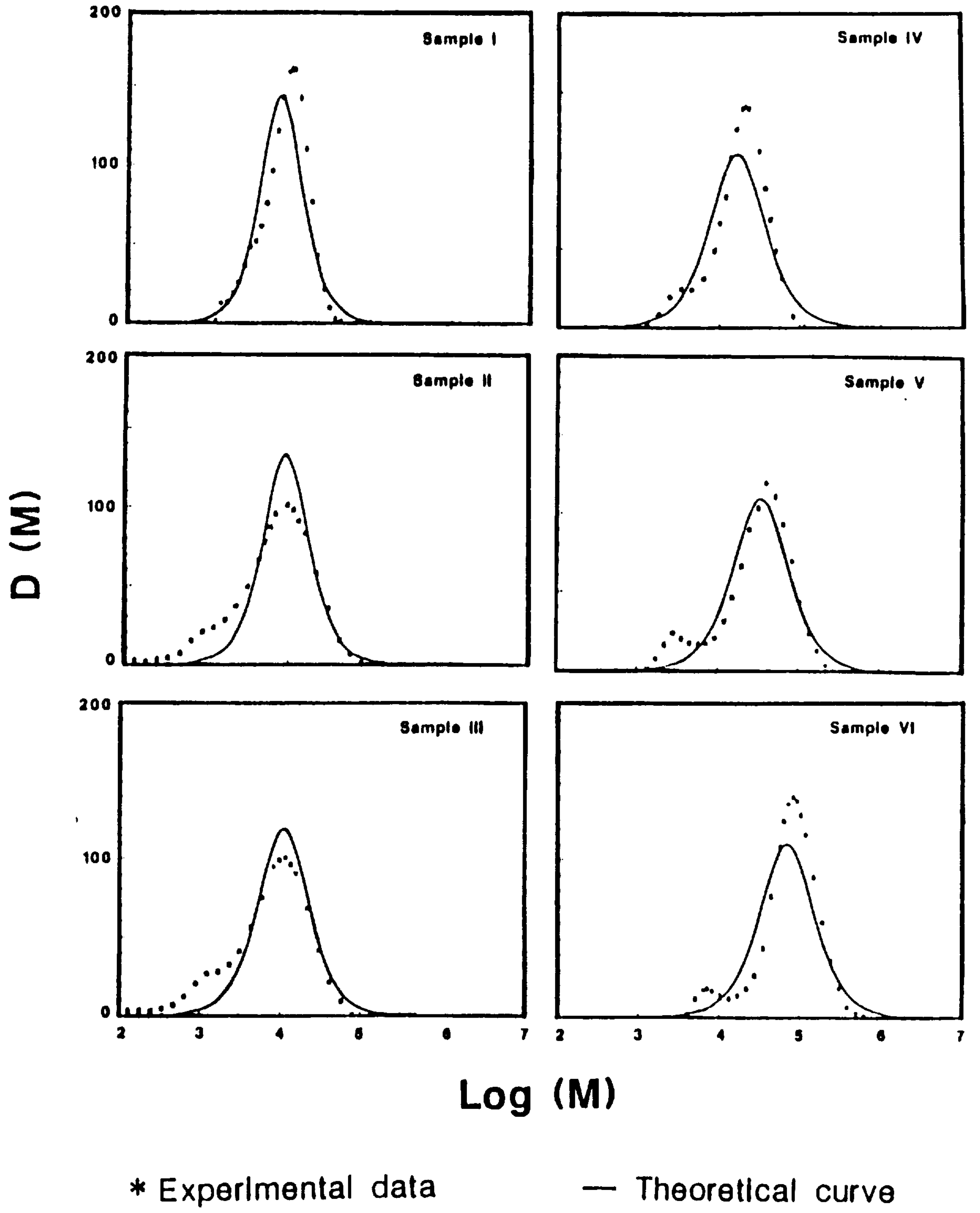


Fig. 6.14 Comparison of the molecular weight distribution curves of six PAE samples between those from GPC method and those by using empirical G'(ω) curve fitting.

weights. The one term curve fitting of Eq. (5.3b) can only simulate single modal distributions of the molecular weights.

6.4.2 Deconvoluting the Relaxation Modulus G(t) to Determine the MW and MWD

6.4.2.1 The Approximation Function of G(t). Equation (5.16) is the approximation function of G(t). Table 6.7 lists τ_j and α_j of all PAE samples for Eq. (5.16) with j = 1. As mentioned before, τ_j is a parameter proportional to the molecular weight and related to the position of the curve. The value of τ_j is closely coincident with B obtained by G' curve fitting. Figure 6.15 is a comparison of log G(t) results as calculated by Eq. (5.16) and obtained from experimental data. It is seen that the theoretical curves are almost like straight lines. Thus, at high relaxation time region, the curves can not fit the experimental data very well.

6.4.2.2 Convertion of the Relaxation Spectrum $H(\tau)$ from τ Scale to M Scale. Equation (5.23) is the relation between the relaxation time and the molecular weight M. The parameter λ and β in Eq. (5.23) are obtained by taking logarithm and applying the least square regression. The value obtained are $\lambda = -18.972$ and $\beta = 3.595$. Thus, we have

$$\log \tau = -18.972 + 3.595 \log M \tag{6.8}$$

where M is the Mw value obtained by the light scattering measurement. When $t = \tau$, the above equation will convert $H(\tau)$ from τ scale to M scale.

Table 6.7 Values of τ_j and α_j parameters of six PAE samples for Eq. (5.16) determined from log G(t) nonlinear curve fitting

Sample	τ_j	α_j
I	0.00004	0.9
II	0.00010	0.85
III	0.00015	0.92
IV	0.002	0.80
V	0.013	0.52
VI	0.18	0.52

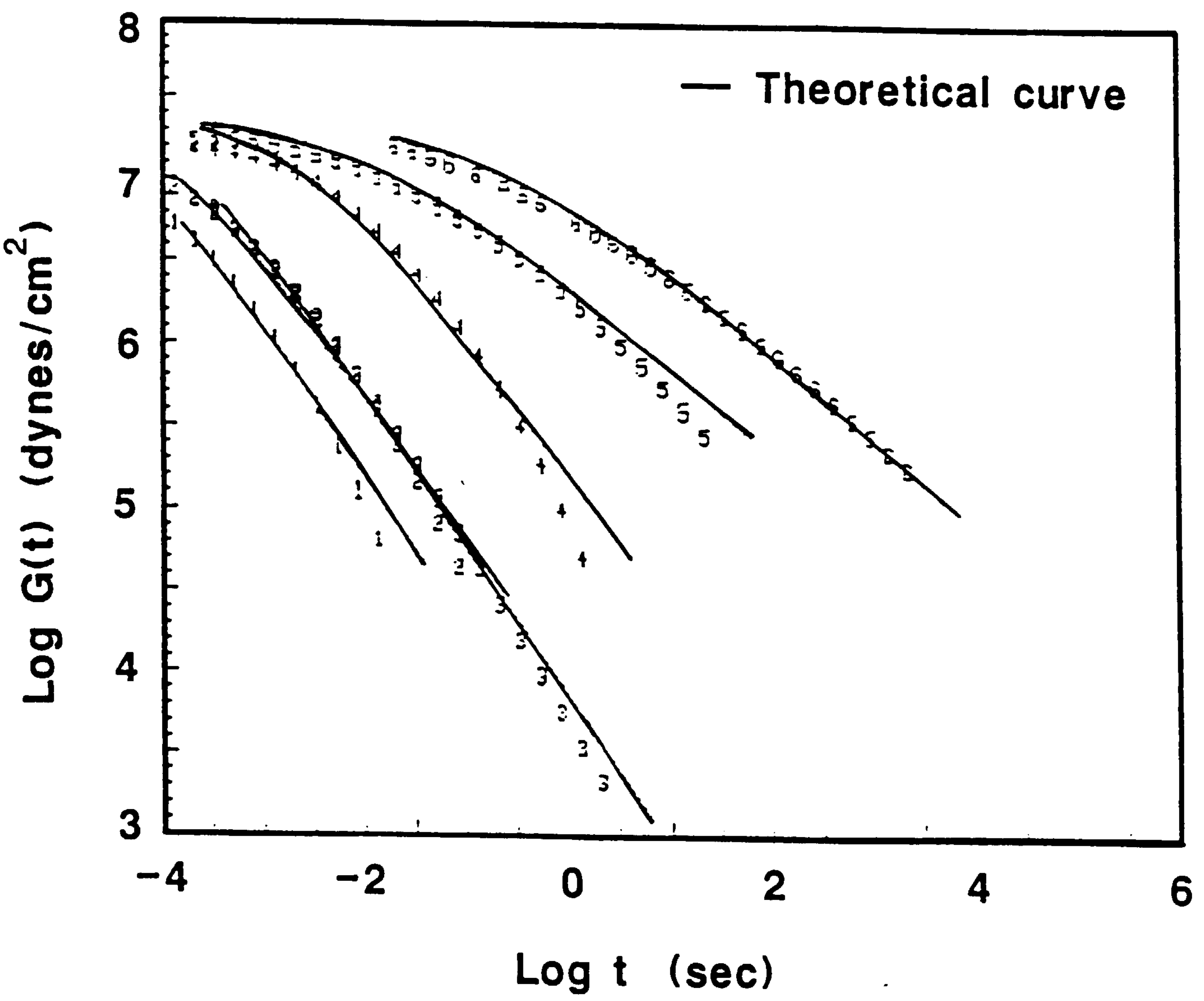


Fig. 6.15 Comparison of log G(t) vs. log t between the theoretical curve and the experimental data.

6.4.2.3 The Calculation of H(M), P(M) and the Scaling Factor S.

The relaxation time spectrum H(M) is calculated by Eq. (5.22), and the volume-fraction differential molecular weight distribution function P(M) is calculated by Eq. (5.18). The Mw and Mn are calculated according to Eq. (5.10) and (5.11) in the same way as discussed before, except the D(M) in Eqs. (5.10) and (5.11) is replaced by P(M).

Table 6.6 summarizes the results of calculated molecular weight. This is compared with the value obtained by GPC and light scattering measurement. The polydispersity ratio Mw/Mn agrees better with the GPC value as compared with that obtained by the G'(ω) curve fitting. The uncertainty of all other samples is within 15%, except samples I and VI. Except sample I, the uncertainty of Mn as compared with GPC value is within 15% as well. The comparison of the simulated MWD curves with those obtained by GPC method is given in Fig. 6.16.

The scaling factor S is calculated here by two different methods, the iteration method and the peak-Mr method. The value of log S changed from 4.9 to 5.12 by iteration method. The value of Mw obtained from GPC is used as the calibration point and the iteration procedures are the same as discussed before. Figure 6.16 shows the results obtained by iteration method.

In peak Mr method,

$$\log S = \log Mw - \log Mr_{peak} \tag{6.9}$$

The value of Mr_{peak} is the M value corresponding to the maximum value of P(M) in the relative Mr scale. The Mw in Eq. (6.9) is the value obtained by GPC method. The results of log S by peak Mr method ranged

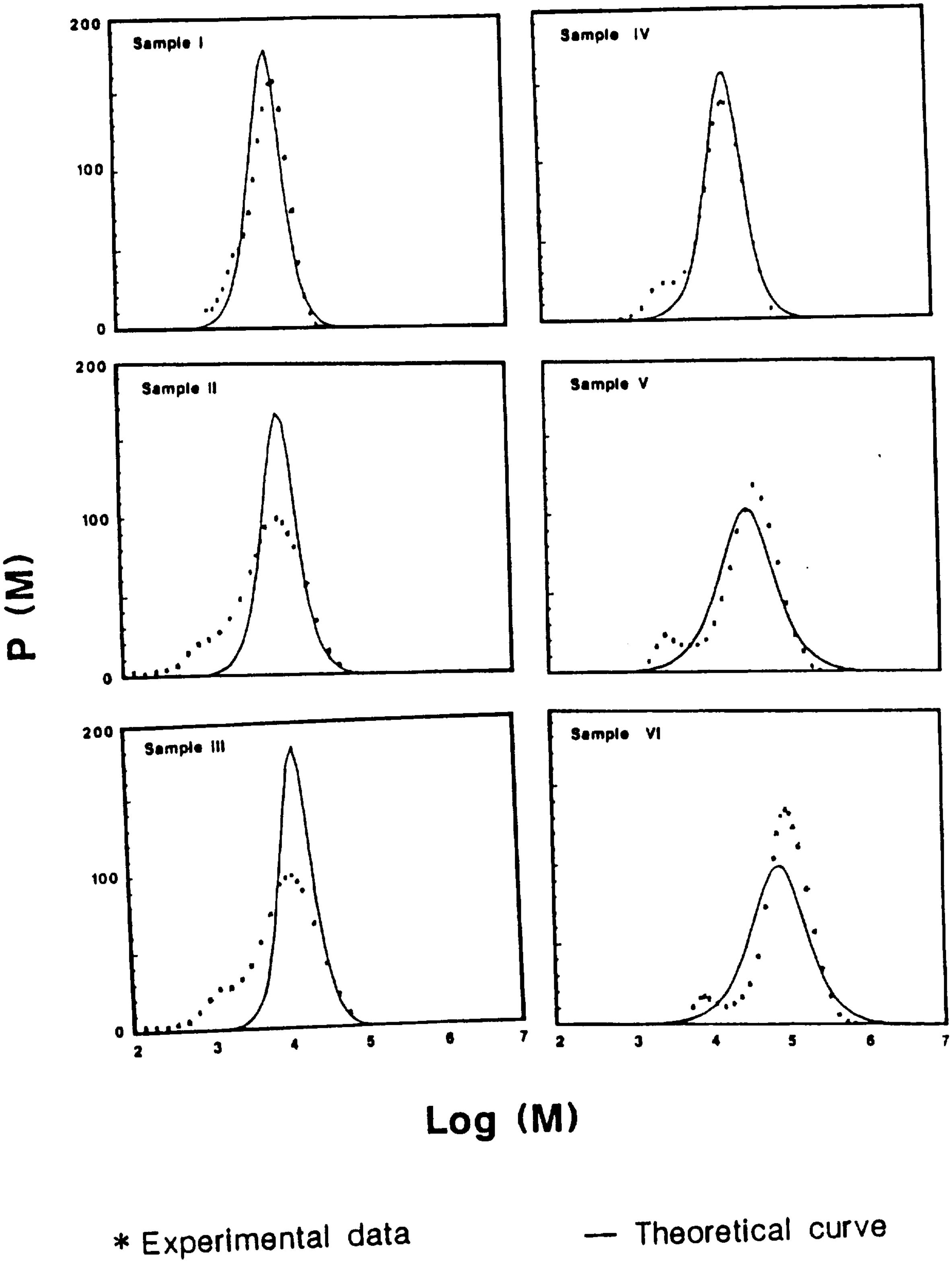


Fig. 6.16 Comparison of the MWD curves of six PAE samples between those from GPC method and those by using empirical G(t) curve fitting with $\beta = 3.595$ and the scaling factor S obtained by iteration method.

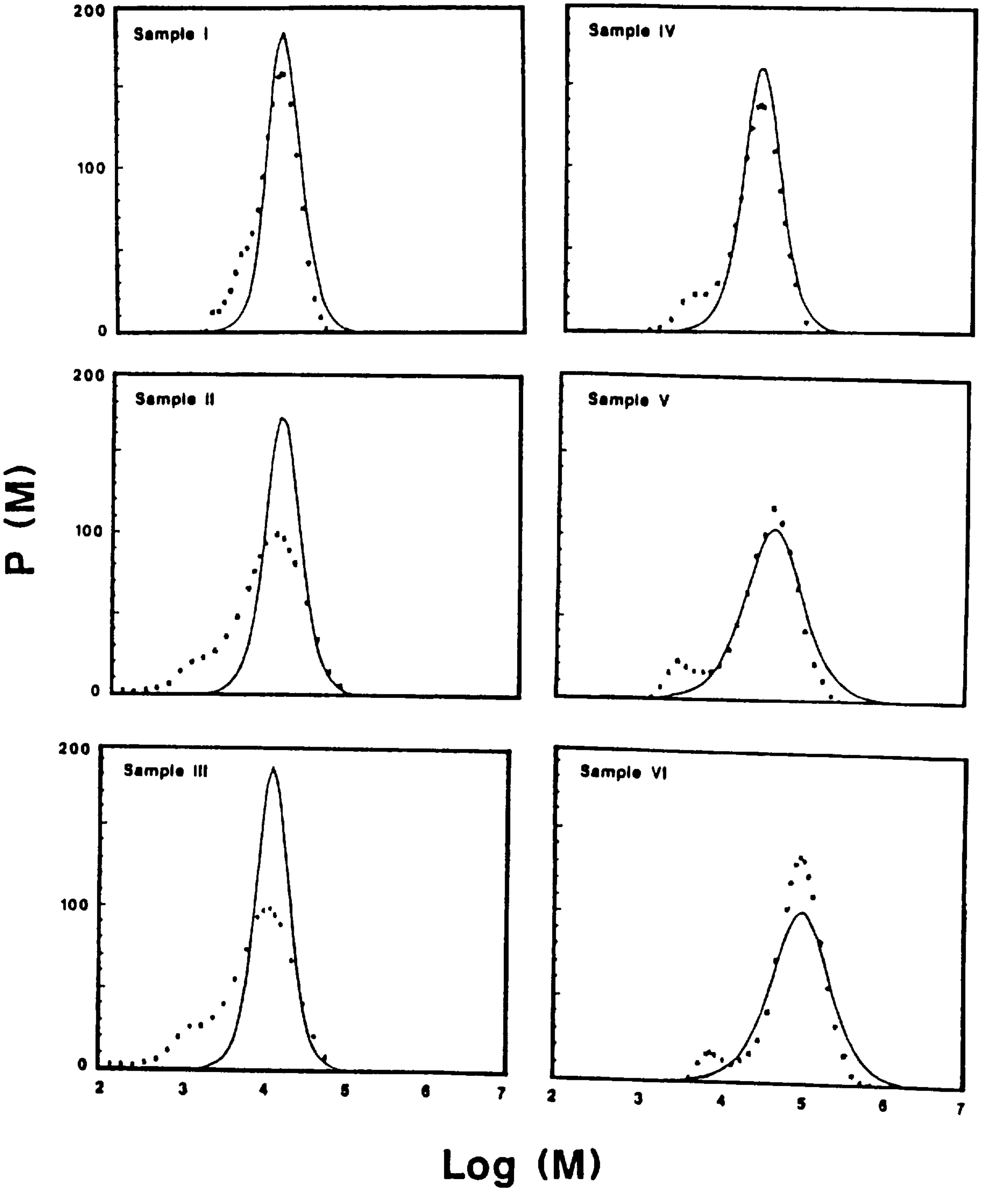
from 5.14 to 5.26. The MWD curves are compared with the results of the GPC method in Fig. 6.17. It can be seen that the molecular weight distribution curve peak fits the GPC data better. But the Mw listed in Table 6.8 does not agree with the GPC value very well, the uncertainty for sampels I, V and VI is more than 25%.

6.4.2.4 <u>Comparison of Different β Value</u>. In both iteration and peak Mr cases, $\beta = 3.595$, obtained by the least squares regression, was used to convert the $H(\tau)$ from τ scale to M scale. For comparison, $\beta = 3.5$ is also used to calculate the MWD curves for all samples. The results are displayed in Fig. 6.18. This is based on the suggestion that the relation between τ and molecular weight M can be expressed as [12, 13]

$$\tau \alpha M^{\beta}, \quad \beta = 3 \quad M>>Mc$$

$$\tau \alpha M^{\beta}, \quad \beta = 3 \quad M<Mc$$

There is no exact method to predict the value of β yet, and it can only be determined experimentally. Wu suggested that $\beta = 3.5$ is preferable [6] for his polystyrene samples and obtained excellent agreement. For PAE samples, $\beta = 3.827$ and $\beta = 3.595$ are obtained by the least square regression in both $G'(\omega)$ and $G(t)$ curve fitting. It looks like $\beta = 3.595$ gives better agreement for PAE samples. From a comparison of the results of MWD for $\beta = 3.595$ and $\beta = 3.5$, it can be seen that the polydispersity Mw/Mn strongly depends on β. If β is increased, the value of Mw/Mn will increase as well, and the polymer will exhibit narrower distribution and vice versa.



* Experimental data -- Theoretical curve

Fig. 6.17 Comparison of MWD curves between those by GPC method and those by using empirical G(t) curve fitting method, with β = 3.595 and the scaling factor is obtained by peak Mr value.

Table 6.8 Molecular weights obtained by Light Scattering, GPC and G(t) curve fitting method with different β and scaling factor S

Sample	Light Scattering	GPC/LALLS			Rheology Method								
					β = 3.5			β = 3.595 (1)			β = 3.595 (2)		
	Mw	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
I	9600	10000±200	4700±200	2.1±0.1	9968	7138	1.40	9949	7253	1.37	12905	9408	1.37
II	17100	13000±2000	6000±2000	2.2±0.5	12928	8860	1.46	13098	9160	1.43	13874	9703	1.43
III	18300	15500±400	10200±200	1.5±0.1	15451	11172	1.38	15631	11500	1.36	14487	10659	1.36
IV	31400	26300±300	16000±2000	1.6±0.2	26441	17177	1.54	26160	17394	1.50	27710	18424	1.50
V	59300	53000±1000	19000±300	2.75±0.02	52550	19144	2.75	52830	20332	2.60	66816	25715	2.60
VI	11300	112000±2000	50000±1000	2.24±0.02	111945	39062	2.87	111687	41320	2.70	143880	53230	2.70

(1) The scaling factor S is obtained by iteration method

(2) The scaling factor S is obtained by peak Mr value method

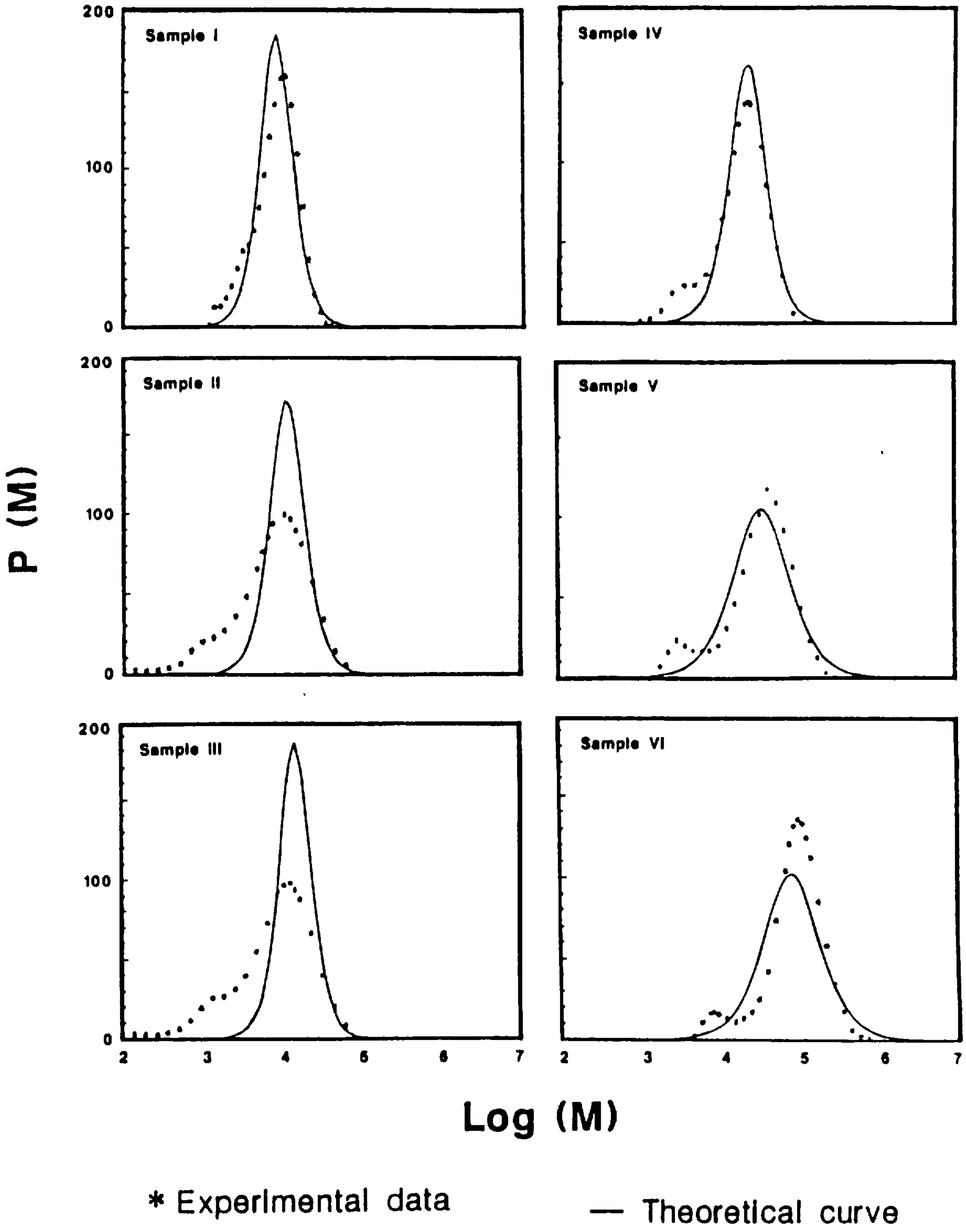


Fig. 6.18 Comparison of MWD curves of six PAE samples between those by GPC method and those by using empirical G(t) curve fitting, with β = 3.5 and the scaling factor S is obtained by iteration method.

Chapter 7

CONCLUSIONS

Several methods of determining the molecular weight and the molecular weight distribution for uncross-linked polymer have been reviewed. The dynamic and relaxation moduli data in terminal and plateau zones are deconvoluted for determination of MW and MWD. It is based on the theory that the dynamic response in the two zones is very sensitive to MW and MWD, and it could be used to obtain the information about MW and MWD. The use of the methods was illustrated with six poly(arylene ether ketone) samples. From this investigation, the following conlusions and recommendations are provided:

1. By shifting and analyzing the dynamic moduli G' and G" master curves of PAE polymers, the information about MW and MWD can be obtained qualitatively. The method of shifting the master curves along the reduced frequency axis is not sensitive to compare the polymers with very close polydispersity ratios Mw/Mn.

2. The molecular weights of two polymers with same molecular weight distribution can be qualitatively determined by shifting the master curves of their dynamic moduli along the frequency axis. The two master curves superimpose in this case and the shift factor is proportional to their molecular weight ratio. The relation used here is $\eta_0 \propto Mw^{5.6}$ for PAE samples. The same method is valid also

for polymers with different MW and different MWD. But the shift factor in this case is obtained by overlapping the G" data in the low frequency limit; the lower G' slope of the shifted curve will indicate a broader MWD.

3. The MW and MWD calculated from the storage modulus $G'(\omega)$ do not agree with the experimental data very well for PAE samples. The uncertainty of Mw/Mn values is up to 30%, and the uncertainty of Mn values is 20%. This may result from the fact that the single modal approximation of G' does not fit the PAE polymers.

4. The method of deconvoluting the relaxation modulus $G(t)$ to determine the MW and MWD gives better results than using $G'(\omega)$ data. The uncertainty of the theoretical results of MW and MWD is within 15% as compared with the experimental data.

5. To convert the molecular weight distribution function from the relaxation time τ scale to molecular weight scale M, the relation

$$\tau = \lambda M^{\beta}$$

can be used. The value of β cannot be predicted exactly. For PAE samples, the least square fitting provides $\beta = 3.595$ in $G(t)$ curve-fitting method, and this provides favorable results. The β value is strongly affected by MWD. The value of β will increase if the MWD is narrower.

6. It is recommended that the present study be extended to simulate the MW and MWD of PAE polymers by using bimodal $G'(\omega)$ and $G(t)$ approximation functions.

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