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LaRC-TPI 1500 SERIES POLYMERS

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Table of Contents

EXPERIMENTAL

RESULTS AND DISCUSSION

FOREWORD

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LaRC-TPI 1500 SERIES POLYMERS*

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ABSTRACT

The crystallization behavior and the melt flow properties of two batches of 1500 series LaRC-TPI polymers from Mitsui Toatsu Chemicals (MTC) have been investigated. The characterization methods include Differential Scanning Calorimetry, the X-ray diffractography and the melt rheology. The as-received materials possess initial crystalline melting peak temperatures of 295 and 305 °C, respectively. These materials are less readily recrystallizable at elevated temperatures when compared to other semicrystalline thermoplastics. For the samples annealed at temperatures below 330°C, a semicrystalline polymer can be obtained. On the other hand, A purely amorphous structure is realized in the samples annealed at temperatures above 330°C. Isothermal crystallization kinetics were studied by means of the simple Avrami equation. The viscoelastic properties at elevated temperatures below and above T_gs of the polymers were measured. Information with regard to the molecule sizes and distributions in these polymers were also extracted from melt rheology.

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*Portions of this work were presented at the 35th International SAMPE Symposium and Exhibition, Anaheim, CA April 2-5, 1990. [1] Supervisor, Polymeric Materials Section. [2] Graduate Research Assistant.

INTRODUCTION

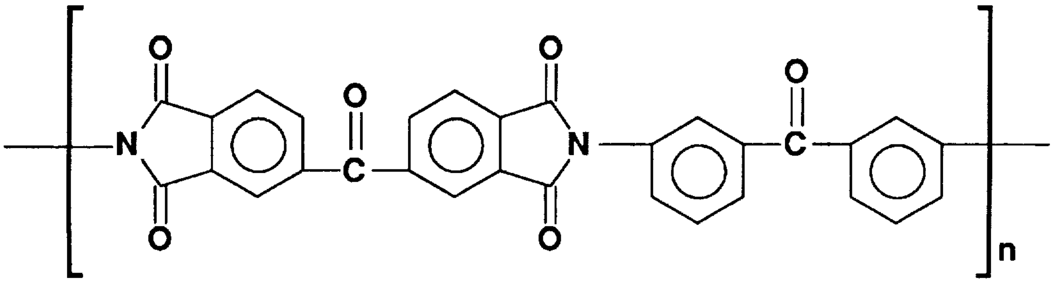
LaRC-TPI (*La*ngley *R*esearch *C*enter - *T*hermoplastic *P*oly*i*mide) is a linear aromatic polyimide. Since its discovery by NASA in the late 1970s [1-5], this material has been developed for a variety of high temperature applications, such as adhesive for bonding metals, insulating fiber and composite design matrix, etc. [6]. In its fully imidized form, however, the relatively poor flow characteristics for this polymer has limited the application. The viscosity at approximately 100°C above its glass transition temperature (T_g = 250 - 260 °C) is at the order of 10^5 - 10^6 Pa-s.

Under a licensing agreement between NASA and Mitsui Toatsu Chemicals, Incorporated (MTC) of Japan, an effort was undertaken to make this high temperature thermoplastic commercially available to the aerospace and electronics industries. A melt endotherm was noted during calorimetric analysis on an earlier version of LaRC-TPI imidized molding powder marketed by MTC [7,8]. The peak temperature of the endotherm for the as-received material was at 272°C. It was found that for the samples annealed at temperatures below 320°C, other semicrystalline forms of the polymer can be obtained, which possess crystal melting peak temperatures between 320-355°C, depending upon the annealing conditions. On the other hand, a purely amorphous structure was realized in the samples annealed at temperatures above 320°C. Such a transient form of crystallinity in the earlier as-received powder afforded beneficial flow properties to the LaRC-TPI polymer system at a relatively low temperature. However, such enhanced flow properties were not gained without sacrificing other aspects of processing. The material was initially composed of partially imidized low molecular weight LaRC-TPI oligomers, which formed crytallization nuclei that provided the enhanced flow characteristics upon melting. The subsequent processing at high temperatures inevitably generated the unwanted volatile by-products from the molecule chain extension/ring closure reactions.

In a continuous effort to improve the processibility, MTC has recently developed a controlled molecular weight LaRC-TPI polymer. Two very processable forms of LaRC-TPI, known as medium flow and high flow 1500 series, have been introduced. These LaRC-TPIs are encapped, which results in minimal volatile reaction by-products being generated in the high temperature processing, such as press and injection molding. The adhesive properties of the medium flow grade material had been reported by Progar et al. [9]. This paper investigates the thermal and rheological properties of these new forms of semicrystalline LaRC-TPI. The characterization methods used include differential scanning calorimetry (DSC), the measurements of X-ray diffraction patterns and the viscoelastic properties.

EXPERIMENTAL

The LaRC-TPI 1500 powders were prepared and supplied by MTC. Samples of two different grades were studied as-received from MTC without further treatments. The medium flow grade material is from lot number 58-704, and is designated hereinafter as MTC-MFG. The high flow grade material, is designated hereinafter as MTC-HFG, and is from lot number 2410. The chemical structure of LaRC-TPI is [1]



LaRC-TPI Chemical Structure

Thermal Properties

A Perkin-Elmer Differential Scanning Calorimeter (DSC) model DSC-7 was used. Samples (3-6 mg) of finely divided polymer were accurately weighed into aluminum sample holders on an analytical balance to 10^{-4} g. A stream of dry nitrogen was continuously flowing over the sample and the reference during measurements. The glass transition temperatures (T_g) and the crystalline melt temperatures (T_m) were determined directly from the thermograms for the samples treated under either isothermal or constant rate of cooling conditions. The heats of fusion were obtained by integrating the areas under the endothermic peaks on the thermograms.

X-Ray Scattering

Wide Angle X-ray Scattering (WAXS) data was obtained on powder specimens of these polyimides. With the X-ray diffractometer operated at 45 kV and 40 mA, using copper radiation with a flat sample holder and a graphite monochromator, the intensity of 1 s counts taken every 0.01° (2θ) was recorded on hard disk for the angular range 5-40° (2θ). An external α-quartz standard was used in goniometer alignment.

Rheological Properties

The melt flow properties of these polymers were characterized by linear viscoelasticity. Measurements were performed on a Rheometrics System IV Rotary Rheometer equipped with a parallel plate test fixture. A sample disc of 2.50 cm in diameter was prepared by molding 0.75 g of material at room temperature under a pressure of 5000 psi. The resulting disc was approximately 1.5 mm in thickness. The sample disc was pre-dried in an oven at 100 °C for at least 24 hours before use. A dynamic motor was used to drive the top plate to oscillate continuously at a specified amplitude, covering a range of frequency from 0.1 to 100 rad/sec. The bottom plate, which remained stationary during measurement, was attached to a torque transducer which recorded forces. During measurement, the plates and test sample were enclosed in a heated chamber purged with nitrogen. The chamber and the plates were preheated to the test temperature before loading the sample disc. This was necessary to obtain a precise gap setting. Measurements were made on each material under isothermal conditions at several selected temperatures between 280 to 380 °C.

Strain (oscillating amplitude) levels were selected to assure that the measurements were performed within the material's linear viscoelastic response range and, at the same time, adequate torque values were generated. Repeatability of the measurements performed at each temperature was checked by varying strain values. Such repeatability is also an indication that sample oxidation effect, if any, is negligible. The recorded cyclic torque values were separated into in-phase and out-of-phase components with respect to the oscillatory deformation imposed on the sample, and the corresponding storage (G') and loss (G") moduli were calculated by the Rheometrics Data Acquisition and Analysis package.

In another experiment, the rectangular torsion mode in the System IV was employed. Dimensions of the samples with rectangular shape were measured as 2.5 x .5 x .045 inches. Strain imposed on the sample was varied manually during the measurement so that the proper torque level could be maintained. Oscillatory frequency was held constant at 10 rad/s. Temperature scans were made at 4°C increments after a 4 minute thermal soak at each measurement temperature. Measurements of the viscoelastic properties were taken at the end of each 4 minute soak. A slight tensional force was always exerted on the sample during the entire course of the temperature scan.

RESULTS AND DISCUSSION

DSC measurements of the as-received LaRC-TPI 1500 materials are shown in Figure 1. Measurements were made at a heating rate of 20°C/min. A single endothermic peak was observed for both MTC-MFG and MTC-HFG samples with slightly different peak temperatures of 305°C and 295°C, respectively.

The endothermic peaks shown in the DSC thermograms represent the meltings of crystallinity in the polymers. The presence of crystallinity in the as-received MTC-MFG sample has been confirmed by X-ray diffractography as shown in Figure 2. The X-ray diffraction pattern reveals the existence of crystalline reflections at various 2θ angles from 5 to 40 degrees. This diffraction pattern is identical to the one previously reported for the as-received sample of LaRC-TPI (lot 72-501) from MTC [8]. This suggests that the MTC-MFG material may have been subjected to a similar thermal post treatment after the cyclodehydration during the manufacturing process.

Also shown in Figure 2 is the diffraction pattern of the MTC-MFG sample which has been annealed at 320°C for 65 hrs. Under this annealing condition, the initial crystallite phase in the as-received material was first melted, and a new (different) crystallite phase was formed. The diffraction pattern of this regenerated crystalline phase is noted to be identical to the one which resulted from higher temperature (such as 320°C) annealing, reported for all of the semi-crystalline LaRC-TPIs studied up to date including samples from MTC, Rogers Corp. and those developed in house by NASA [8].

Heat of fusion for the MTC-HFG sample ($\Delta H = 46.8$ J/g) was about 15% higher than MTC-MFG sample ($\Delta H = 39.3$ J/g). The T_g s were not readily detectable from DSC scans for both as-received materials. It was also found that less than 5% weight loss was recorded for both materials by the thermogravimetric (TGA) measurement during a programmed temperature scan up to 500°C.

Overall Crystallization Behavior

Unlike other thermoplastics, such as Poly(aryl-Ether-Ether-Ketone) (PEEK), the LaRC-TPI 1500 polymers are not readily recrystallizable after the melting of the initial crystalline phase during a number of single thermal treatments at various conditions. When a sample was heated from room temperature (RT), at a rate of 20°C/min, to several temperatures higher than the initial crystalline melting peak temperatures, and followed by a rapid quench, neither the presence of crystallization exotherm peaks during the initial scan, nor the existence of crystalline melting endothermic peaks during the second scan after the quench, were evident.

Investigations of the recrystallization behavior of the LaRC-TPI 1500 polymers treated under prolonged isothermal annealing were conducted by DSC. As-received powder was first heated at a rate of 20°C/min from RT to a specified temperature above the initial melting point (295 or 305°C). After the completion of various hold times at that temperature, a rapid quench to ambient temperature followed. Subsequent thermograms were obtained by rescanning the quenched samples at a rate of 20°C/min from RT to 400 °C. Typical thermograms obtained for MTC-MFG samples after various hold times at 310°C are shown in Figure 3. The characteristic of bimodal melting peaks becomes more evident as the annealing time becomes longer. Both peaks, which occured at temperatures of 327 and 341°C, respectively, were higher than the annealing temperature (310°C). Unlike the recrystallization behavior observed for MTC LaRC-TPI lot 72-501 samples [7], the peak melting temperatures did not increase significantly with the increasing annealing times. The T_g s were also evident from the thermograms for all annealed samples. $T_g =$ 242°C was found to stay the same, independent of annealing times. This value of T_g was lower than the nominal 260°C attainable under similar annealing condition for other versions of the Mitsui LaRC-TPI polymers studied before.

The thermograms obtained after various annealing times at 320°C and 330 °C are shown in Figures 4 and 5, respectively. Characteristics similar to those discussed above for the samples annealed at 310°C were observed. Higher crystalline melt peak temperatures were reached, as expected, with increasing annealing temperatures. In the case of 330°C annealing, the peak of the higher melting temperature gradually became less evident as the annealing time became longer. The position of the peak temperatures, however, remained stable independent of annealing times. Peak melting temperatures and the heat of fusion are tabulated in Tables 1 and 2, respectively. It is also noted that the T_g remained approximately the same at 242 °C for samples annealed under all three temperatures.

The recrystallization behavior of MTC-HFG samples annealed at 320°C is shown in Figure 6. The heat of fusion and the crystalline melting peak temperatures are tabulated in Table 3 which includes other two annealing temperatures as well. Examining these figures and tables, it is noted that, after thermal treatments of prolonged annealing conditions investigated, the recrystallization thermograms of the DSC and the glass transition temperatutes for the MTC-MFG and the MTC-HFG polymers, were nearly indistinguishable.

The behavior of the T_g for the 1500 series samples with respect to the annealing temperature and time were quite different from those previously reported for other versions of MTC LaRC-TPI [7]. For example, an increase of over 20°C in T_g was observed for the lot 72-501 sample annealed at 320°C for 60 minutes. The stable T_g for the 1500 series LaRC-TPI was an indication of a relatively stable amorphous region in the material, and is attributed to the controlled molecular weight through end capping of molecules. Values of T_g as high as 248°C are observed in Figure 7 for a series 1500 sample annealed at 380°C for 1 hr.

The overall crystallization behavior discussed above is observed only for the LaRC-TPI 1500 series powder annealed isothermally at temperatures below 330°C. At annealing temperatures higher than 330°C, there were no crystalline melting peaks that could be detected.

The crystallization behavior for the samples treated under constant rate of cooling conditions were also investigated. As-received powder was first scanned at a rate of 20°C/min from RT to 320°C. A constant rate of cooling (2°C/min) was then immediately employed until ambient temperature was regained. A subsequent thermogram was obtained by rescanning the sample up to 400°C at a rate of 20°C/min. Unlike the LaRC-TPI sample from lot 72-501 studied before [7], no crystalline melting endotherm was evident during the second scan.

Kinetics of Isothermal Recrystallization Reaction

Crystallization kinetics are commonly analyzed by means of the Avrami equation [10, 11].

$$\chi_t = 1 - \exp(-Z t^n) \qquad (1)$$

where χ_t is the weight fraction of crystallized material at time t, Z, a rate constant, and n, the Avrami exponent.

There is considerable doubt as to the validity of a simple Avrami equation alone describing the total crystallization behavior of bulk polymers. Despite this, however, analyses based upon Eq. (1) are justified, as a means of comparison, but the values of the parameters Z and n may have no mechanistic significances. Equation (1) can be rearranged as:

$$\mathrm{Log}[-\mathrm{Ln}(1-\chi_t)] = \mathrm{Log}\, Z + n\ \mathrm{Log}\, t \qquad (2)$$

The Avrami parameters can then be conveniently extracted from the slope and intercept of the straight line in a plot of Log [- Ln (1 - χ_t)] vs. Log t.

Measurements of crystallization exotherms are restricted by the sensitivity of the calorimeter and the limit of sample size. For the LaRC-TPI series 1500 powders studied here, the slow crystallization rates make the crystallization exotherms difficult to trace. It is possible, however, to study the kinetics of crystallization by measuring the crystallinity developed in various time intervals from the area under the endotherms produced on subsequent melting as shown by Figures 3, 4 and 5. This method is more time consuming and less accurate. It was reported, however, to give very similar crystallization isotherms to that of direct measurement in the study of polyethylene crystallization kinetics [12].

Plots of Eq. (2) for the MTC-MFG LaRC-TPI powders treated isothermally at three temperatures are shown in Figure 8. A straight line can be satisfactorily determined by the least squares fit for each set of data. The Avrami parameters extracted from the fits are tabulated in Table 4. Also included in Table 4 are those reported previously for LaRC-TPI lot 72-501 samples [7]. It is noted that the *n* values are fractional but independent of annealing temperatures. The crystallization rate constant, Z, was much smaller for the series 1500 LaRC-TPI polymer.

Comparisons between Eq. (1) and the experimental data are shown in Figure 9. The agreements are considered satisfactory. It can be seen that among the three annealing temperatures studied here, T = 330°C was the least favorable crystallization temperature for the material. The fastest crystallization reaction rate occured, however, at 310°C as can be seen in this figure.

Melt Rheology

Unlike samples of earlier versions of LaRC-TPI from MTC, the as-received 1500 series polymers were relatively stable in the hot melt processing. Figure 10 shows the thermal stability of these two polymers annealed at 350°C. Measurements were made by the parallel-plate small amplitude dynamic experiments, with angular frequency of $\omega = 10$ rad/sec and strain of 10% in the Rheometrics System IV rheometer. Two linear viscoelastic properties, i.e., the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, were directly obtainable. The complex viscosity, η^*, was calculated from

$$\eta^* (\omega) = G^*(\omega)/\omega = [G'(\omega)^2 + G''(\omega)^2]^{1/2} /\omega \qquad (3)$$

The initial drops in the linear viscoelastic properties, as noted in Figure 10, were attributed to the temperature effects. Sample MTC-MFG exhibited a higher level of thermal stability than that of the MTC-HFG sample. Within the duration of the measurement, the MTC-MFG polymer was essentially unchanged, while an increase from 8×10^3 to 4.5×10^4 dynes/cm^2 in $G'(t)$ was observed for the MTC-HFG polymer. For a comparison of thermal stability, an increase of over 3 orders of magnitude in $G'(t)$ was reported for MTC LaRC-TPI lot 72-501 sample [13].

It has been noted that $|\eta^*(\omega)|$ closely resembled $\eta(\dot{\gamma})$, in which $\eta(\dot{\gamma})$ is the steady shear viscosity at shear rate $\dot{\gamma}$. The relationship $\eta(\dot{\gamma}) = \eta^*(\omega)$ is known as the Cox-Merz rule [14]. It has been proven very useful in predicting $\eta(\dot{\gamma})$ when only linear viscoelastic data are available [15]. Complex viscosities of both MTC-MFG and MTC-HFG LaRC-TPI polymers measured between 280 - 380°C are shown in Figure 11. At approximately 100°C (T = 340°C) above the glass transition temperature (T_g = 242°C) of the polymers, the zero shear viscosities were 10^4 and 2 x 10^3 Pa secs for the MTC-MFG and the MTG-HFG polymers, respectively.

Master curves of $\eta_p^*(\omega_p)$, $G_p'(\omega_p)$ and $G_p''(\omega_p)$ are shown in Figures 12 and 13 for both grades of series 1500 LaRC-TPI. These curves were constructed based on the principle of time-temperature superposition [16]:

$$Q_p\ (\omega_p, T_r) = Q\ (\omega, T) \tag{4a}$$

$$Q_p = Q\ T_r\,\rho_r / T\,\rho \tag{4b}$$

with $\omega_p = \omega\ a_T$, where a_T is the shift factor, ρ is the density and Q represents any linear viscoelastic property. The reference temperature was selected at T_r = 320°C. The resultant shift factors, a_T (T), as tabulated in Table 5 for these two polymers, can be well illustrated by the WLF theory [16], as shown in Figure 14, with the two material parameters C_1 and C_2 included in Table 5 as well. It is noted that a_T is independent of M_w and molecular weight distribution (MWD). This behavior indicates that, for the polymers of LaRC-TPI under investigation, the molecular weights were at levels above the critical molecular weight, M_c, at which the entanglement effect becomes evident [17, 18]. According to the following formula:

$$E_\eta = 2.303\ (C_1 / C_2)\ R\ T_r^2 \tag{5}$$

where R is the universal gas constant, the activation energy for viscous flow is E_η = 69.8 kcal/mole for these polymers. The master curves extend the frequency range from three to six orders of magnitude as shown in the Figures. $G_p'(\omega_p)$ and $G_p''(\omega_p)$ include the melt flow or terminal zones in the lower frequency region and extend into the high frequency regime where the beginning of rubbery zones become visible.

It is well established that the rheological properties of polymer melts are dependent on the weight average molecular weight ($\overline{M}_w$) and the molecular weight distribution (MWD) [16, 19, 20]. The rheological properties obtained from the dynamic measurements can be related to molecular structure. The frequency dependence of the dynamic moduli ($G'(\omega)$ and $G''(\omega)$) is dependent on the distribution of relaxation times. For linear polymers, such as the LaRC-TPI, with no long chain branching, this is governed by the distribution of molecular weights. Some observations with regard to the $\overline{M}_w$ and MWD of these two polymers can be made from the master curves of $G_p'(\omega_p)$ and $G_p''(\omega_p)$ of Figure 13 as follows:

(i) The broad transitions from the terminal to the rubbery zone are indications of broad MWD possessed by these polymers. The extension of the terminal zone of sample MTC-MFG further into the lower frequency regions indicates that the MTC-MFG polymer has a higher $\overline{M}_w$ than the MTC-HFG material.

(ii) In the terminal zone (i.e., lower frequency regime), the theory of linear viscoelasticity gives

$$\lim_{\omega \to o} G_p''(\omega_p) = \eta_o \, \omega_p \tag{6}$$

$$\lim_{\omega \to o} G_p'(\omega_p) = \eta_o^2 \, J_e^o \, \omega_p^2 \tag{7}$$

where η_o is the zero shear viscosity and J_e^o is the steady state compliance of the material. It had been experimentally established that η_o is governed by the longest relaxation time, and is related to $\overline{M}_w^{\alpha}$, independent of MWD for many high polymers. α equals 1 for polymers with low $\overline{M}_w$. For polymers of flexible backbone chains, with $\overline{M}_w > M_c$, where M_c is the critical molecular weight for entanglement effects to become dominant, α becomes 3.4. For molecules with stiff backbone chains, however, higher values of α (5.0 - 5.5) were reported for aromatic polymers [18, 21]. J_e^o accounts for the elasticity of the macromolecules. Because of the sensitivity of this quantity to the subtle differences in the MWD, especially in the high molecular weight tail, J_e^o is usually related to the ratio of a higher moment in molecular weights, such as the polydispersity ratio $\overline{M}_w / \overline{M}_n$.

Based on these observations, a reduced variable was introduced by Zeichner et al. [22, 23] to eliminate viscosity (or equivalently $\overline{M}_w$) differences between polymers. The reduced frequency was defined as $\omega_R = \eta_o \, \omega_p$. By shifting the $G_p'(\omega_p)$ and $G_p''(\omega_p)$ master curves along the reduced frequency axis, polymers with identical MWD will superimpose one on the other, irrespective of the differences in $\overline{M}_w$s. For polymers having different MWDs, by overlapping the $G_p''(\omega_R)$ curves at the regime of low frequency ends, the rest of the curves will not be superimposable. Instead, broader MWD polymers will exhibit master curves with lower slopes in the transition regime between terminal and rubbery zones.

For the LaRC-TPIs presently studied, we have $\eta_o = 1.13 \times 10^4$ and 4.83×10^4 Pa secs for MTC-HFG and MTC-MFG samples, respectively, at 320°C. The master curves, $G_p'(\omega_R)$ and $G_p''(\omega_R)$, constructed with respect to the reduced frequency ω_R are shown in Figure 15. It is noted that the master curves of both materials are superimposable over a broad frequency scale. This suggests that an identical MWD exists in these two polymers.

(iii) Based on the same observations stated in (ii) for the viscoelastic behavior of high polymers with respect to the $\overline{M}_w$ and MWD, Dormier et al. [24] suggested to shift the $G_p''(\omega_p)$ curves directly for the resins to be compared, such that the best possible superposition is obtained at the lowest frequencies measured. This shifting procedure removes the effect of differences in η_o (i.e., $\overline{M}_w$). The extent of overlap for both $G_p'(\omega_p)$ and $G_p''(\omega_p)$ for data shifted in this fashion may then be interpreted in terms of relative $\overline{M}_w$ and MWD.

Dormier et al. proposed, in particular, that the frequency shift, a_m, needed to overlap the low frequency (long relaxation time) ends of $G_p''(\omega_p)$ curves could be used to estimate the ratio of $\overline{M}_w$s by

$$(\overline{M}_w)_h / (\overline{M}_w)_l = (a_m)^{1/\alpha} \tag{8}$$

where h and l denote samples with the higher and lower molecular weights. Measurements of GPC and rheological properties on a series of polyethylenes [24] with various $\overline{M}_w$ and MWD had confirmed the validity of Eq. (8) with $\alpha = 3.4$.

For the series 1500 LaRC-TPIs studied here, the shifted master curves of $G_p'(\omega_p)$ and $G_p''(\omega_p)$ for both polymers are shown in Figure 16. It can be noted that the master curves are superimposable over a broad range in frequency scale. This also confirms the conclusions made in (ii) above that an identical MWD profile exists in both of these polymers. The shift factor was found to be $a_m = 4.8$, which gives a ratio of $(\overline{M}_w)_{MFG} / (\overline{M}_w)_{HFG} = 1.6$ and 1.4 with $\alpha = 3.4$ and 5.0, respectively, for these two grades of LaRC-TPI. Such information with regard to the molecular weights and the distributions, extracted from the rheological properties of the LaRC-TPI polymers as discussed above, compares favorably to those provided by MTC*, where an identical polydispersity of 3.0 and a ratio of $(\overline{M}_w)_{MFG} / (\overline{M}_w)_{HFG} = 1.27$ were obtained from the Low Angle Laser Light Scattering (LALLS) measurements for these two grades of 1500 series LaRC-TPI.

*Private communications with Dr. Terry L. St. Clair, NASA LaRC

Viscoelastic Properties of Solid Samples

The complex modulus, G^*, measured by the rheometer during a temperature scan at a fixed frequency of 10 rad/s is shown in Figure 17. Amorphous samples of both MFG and HFG polymers were fabricated by compression molding. Test specimens with rectangular shapes were then cut from the 3" x 3" molded pieces. It can be seen from the figure that the temperature ranges in the glass transition, which occured around 260°C, covered 40-60°C. Below T_g, the moduli were at approximately 1 - 2 x 10^{10} dynes/cm^2 level typical for such high performance materials. After T_g, a drop of more than 3 orders of magnitude in moduli was evident for both grades of polymers.

Also included for comparison in Figure 17 are the viscoelastic properties of semicrystalline Poly(aryl-Ether-Ether-Ketone) (PEEK) and the other versions of Mitsui LaRC-TPI documented before in the literature [7]. The amorphous and semicrystalline LaRC-TPI samples [7] were molded from the Mitsui lot 72-501 powders, in which the oligomers were not encapped. Thus, unlike 1500 series polymers, the molecular weights in the molded samples were not controlled. It is seen that after the glass transition, the modulus of the amorphous sample dropped only approximately two orders of magnitude, which is an indication that the molded samples fabricated from lot 72-501 possessed higher molecular weights than the 1500 series materials. The higher moduli after T_g observed for the semicrystalline (PEEK and LaRC-TPI) samples are attributed to the crystallinities in those samples. The glass transition temperatures of PEEK, reported at 145°C, is however seen to be significantly lower than the nominal T_g of 260°C possessed by the LaRC-TPI material.

CONCLUSIONS

The thermal properties, crystallization behavior and the melt rheology of two batches of series 1500 LaRC-TPI polymer have been characterized. These materials were supplied by Mitsui Toatsu Chemical, Inc. (MTC) of Japan. The use of molecule endcapping during synthesis distinguished these polymers from all the previous versions of LaRC-TPI from MTC, and made these polymers more stable with less reaction by-product generation in the subsequent hot melt processing.

A transient form of crystallinity was found in the as-received polymers. The diffraction patterns measured by WAXS was identical to the one found previously in the other as-received LaRC-TPI powders from MTC, which suggested that these materials may have been subjected to similar thermal post treatment after the cyclodehydration during the manufacturing process.

The as-received powders are less readily recrystallizable at temperatures above their initial melting peak temperatures when compared to other semicrystalline thermoplastics. For the samples annealed at temperatures below 330°C, a semicrystalline polymer was obtained. On the other hand, a purely amorphous structure was realized in the samples annealed at temperatures above 330°C.

Isothermal crystallization kinetics were studied at 310, 320 and 330°C by means of the simple Avrami equation. The Avrami exponent constants, n, were found to be fractional and independent of annealing temperatures. The rate constants of crystallization were found to decrease with increasing annealing temperatures, and were much slower (about three orders of magnitude samller) than those reported for other versions of LaRC-TPI from MTC.

Melt rheology measurements indicated these materials should be very processable. At approximately 100°C above the glass transition temperature of the polymers (T=340°C), the zero shear viscosities are in the range of 10^3 - 10^4 Pa secs. Master curves of the storage and the loss moduli were constructed by the principle of time-temperature superposition, and the shift factors were satisfactorily explained by the WLF theory. Comparing the viscoelastic master curves of theses two polymers, an analysis was performed which revealed that a factor of 1.4 difference in the weight average molecular weights existed between these two batches of 1500 series LaRC-TPI polymers. These two polymers were also shown by the rheological measurements to possess identical molecular weight distributions.

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Table 1. Peak Crystalline Melting Temperatures (°C) for 1500 Series MTC-MFG Samples Annealed Under Various Isothermal Conditions

t (Minutes)	310°C		320°C		330°C	
15	---,	337.3	---,	339.9	---,	346.0
30	---,	340.0	---,	343.0	---,	346.7
45	---,	341.0	---,	344.6	---,	348.6
60	327.3,	341.7	---,	346.5	---,	350.7
90	327.5,	342.7	338.2,	347.9	---,	352.3
120	327.5,	342.6	338.2,	347.8	347.7,	352.3
180	327.5,	342.6	338.2,	348.3	346.3,	351.8
240	327.5,	342.7	---	---	346.9,	353.6
300	---	---	338.9,	347.7	---	
360	---	---	---	---	346.9,	354.5

Table 2. Heat of Fusion (J / g) For 1500 Series MTC-MFG Samples Annealed Under Various Isothermal Conditions.

t (Minutes)	310°C	320°C	330°C
15	0.40	0.47	0.13
30	1.54	1.86	0.58
45	3.65	3.67	1.26
60	8.51	7.97	2.58
90	21.92	22.28	7.51
120	29.30	27.69	16.39
180	31.80	31.08	27.00
240	33.93	---	29.07
300	---	32.33	---
360	---	---	29.67

Table 3. Heat of Fusion and Crystalline Peak Melting Temperature for 1500 series MTC-HFG Samples Annealed under Various Isothermal Conditions

t (mins)	310°C		320°C		330°C	
	ΔH(J/g)	T_m(°C)	ΔH(J/g)	T_m(°C)	ΔH(J/g)	T_m(°C)
120	---	---	30.87	347.2	---	---
180	34.55	327.5, 342.7	31.54	338.5, 347.2	27.70	346.0, 353.2
300	35.20	327.5, 342.1	32.04	338.2, 347.0	28.77	346.5, 353.7

Table 4. Avrami Parameters for Isothermal Crystallization Reaction of LaRC-TPI Powders.

Sample	T(°C)	n	$Z \times 10^2 \, (\mathrm{min}^2)^{1/n}$
Lot 72-510 [7]	280	1.033	7.75
	300	1.101	4.86
	320	1.109	3.73
Lot 58-704 (1500 Series, MTC-MFG)	310	2.50	0.00117
	320	2.644	0.00062
	330	2.707	0.00016

Table 5. Shift Factors a_T and Material Parameters C_1 and C_2 of the WLF Equation for LaRC-TPI 1500 Series Polymers

T (°C)	a_T, MTC-MFG	a_T, MTC-HFG
280	---	134.6
290	31.4	---
300	9.1	9.8
320	1.0	1.0
340	0.17	0.17
360	0.03	0.035
380	0.0082	0.0102
C_1	10.37	8.59
C_2	238.79	198.60

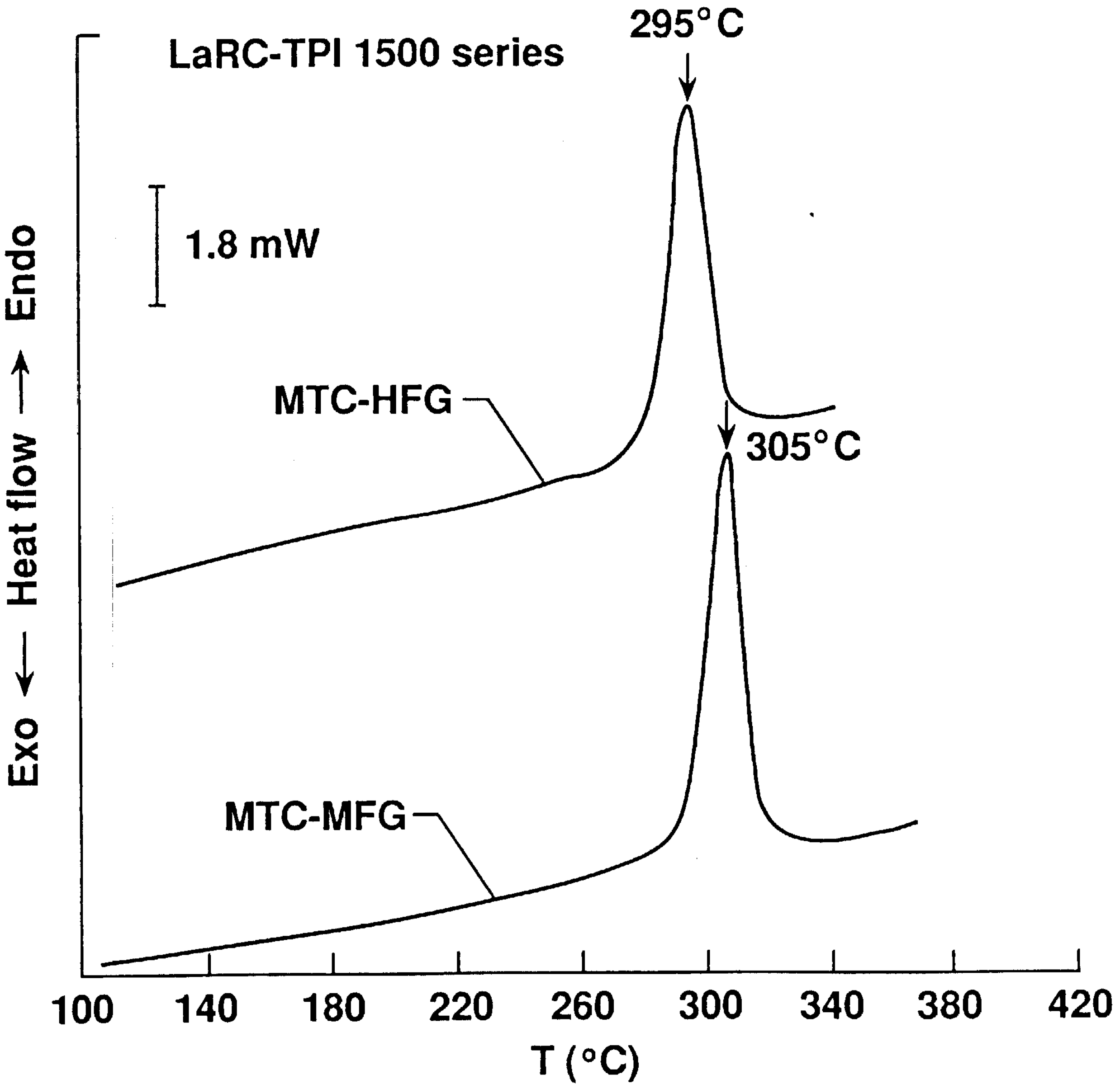

Figure 1. DSC thermograms of the as-received MTC-HFG and MTC-MFG LaRC-TPI 1500 series polymers.

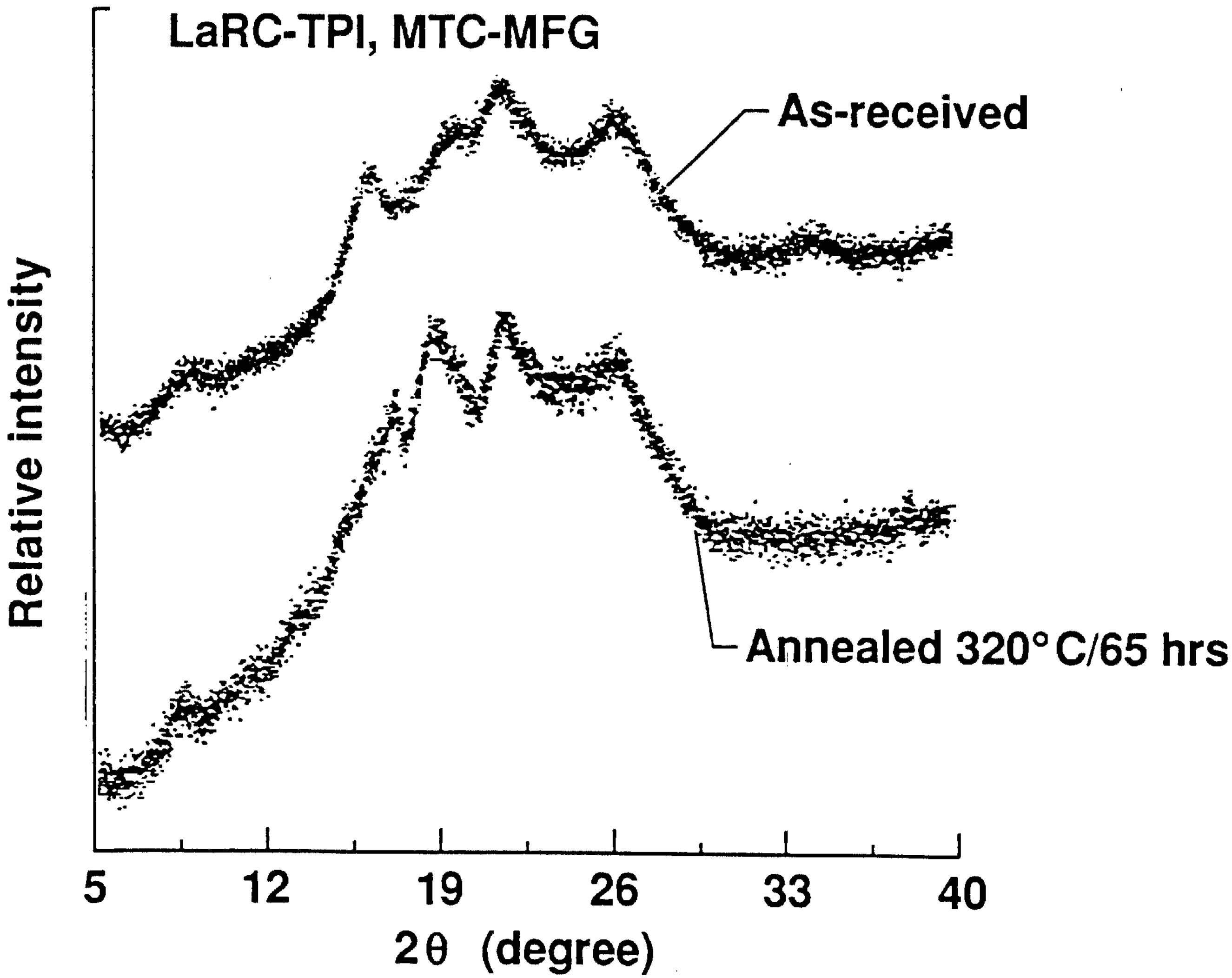

Figure 2. X-ray diffractographies for the crystalline phases in the as-received and the annealed samples of MTC-MFG polymer.

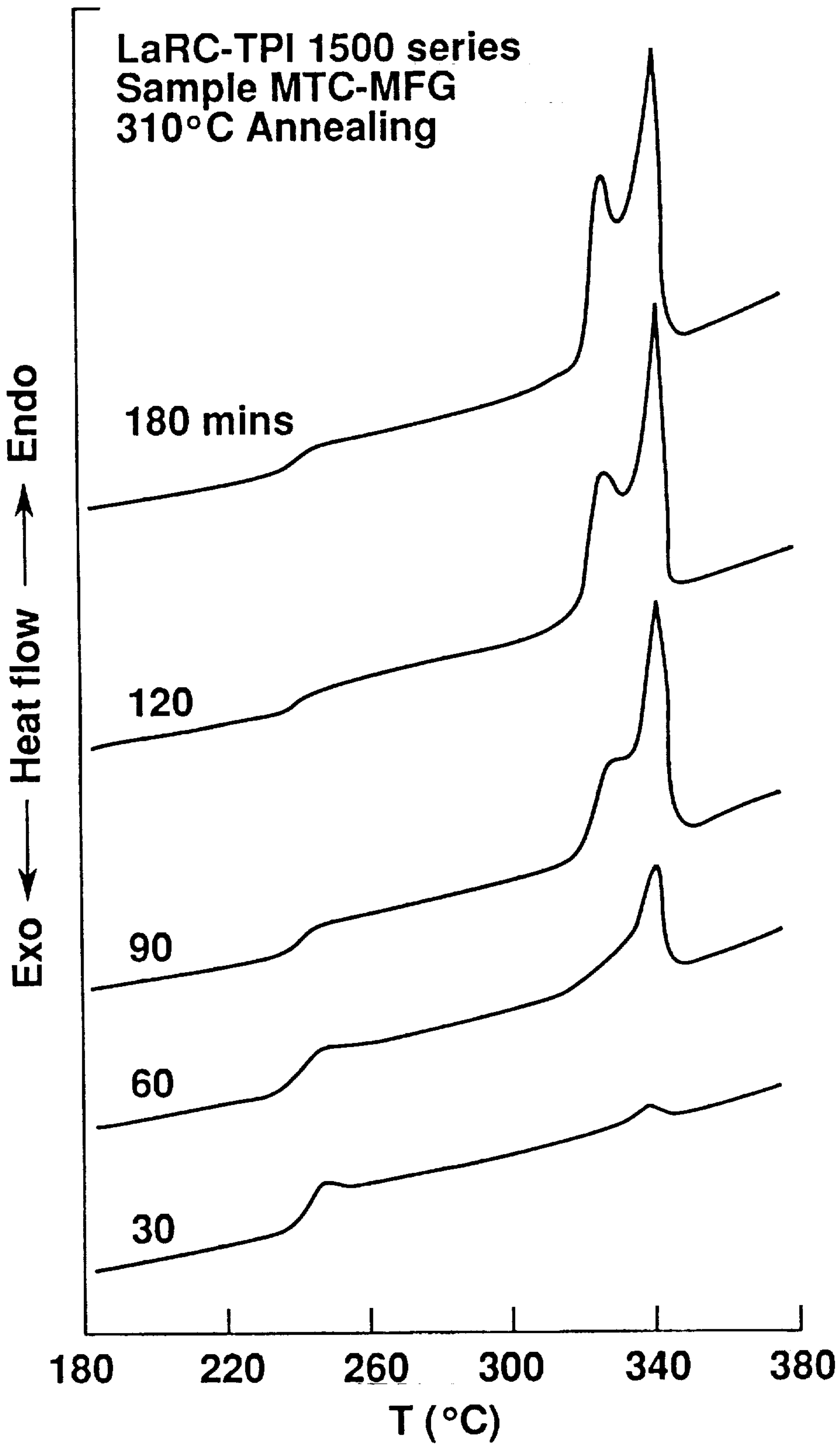

Figure 3. DSC thermograms for the MTC-MFG polymer annealed at 310°C for various lengths of time indicated.

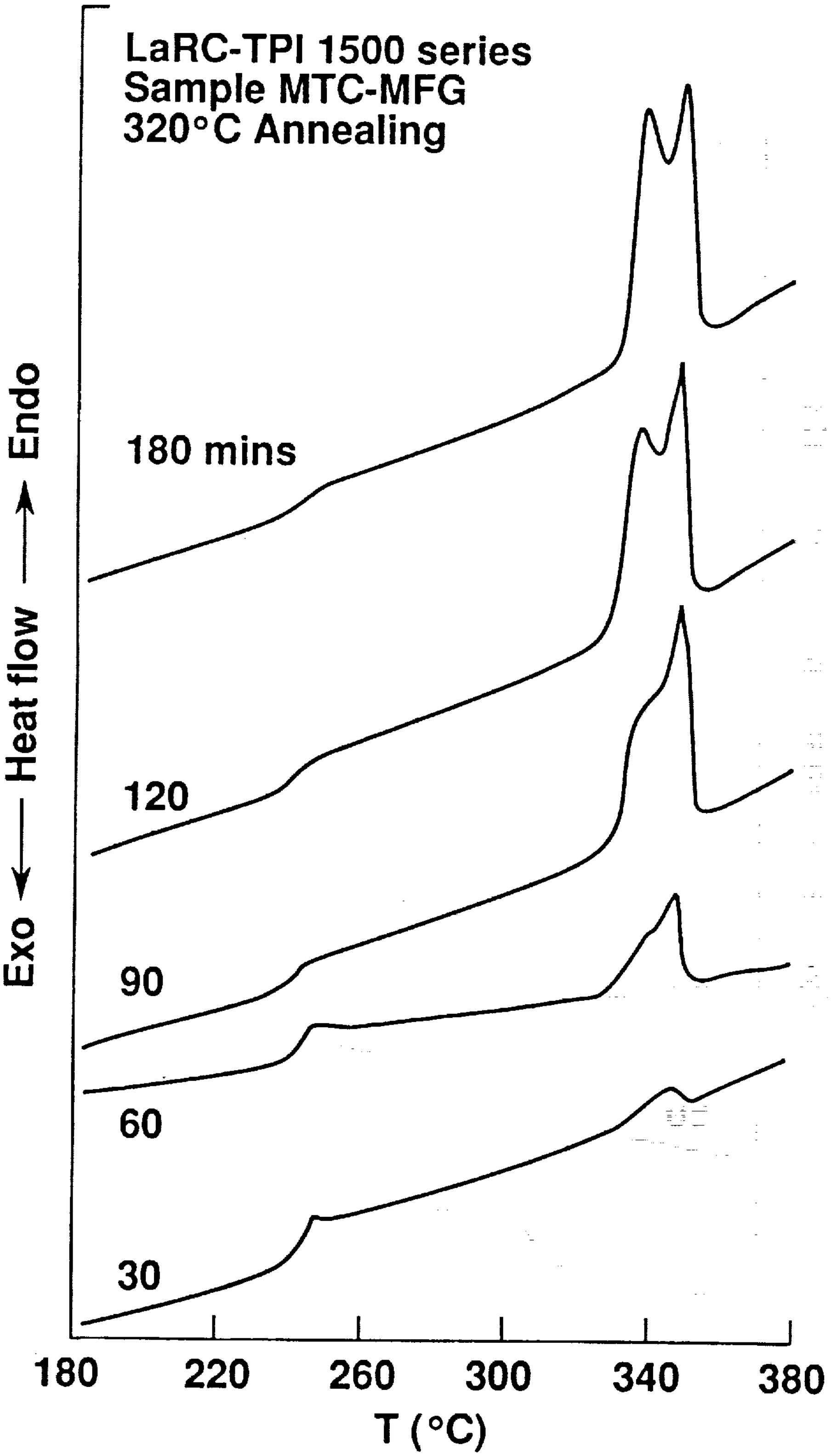

Figure 4. DSC thermograms for the MTC-MFG polymer annealed at 320°C for various lengths of time indicated.

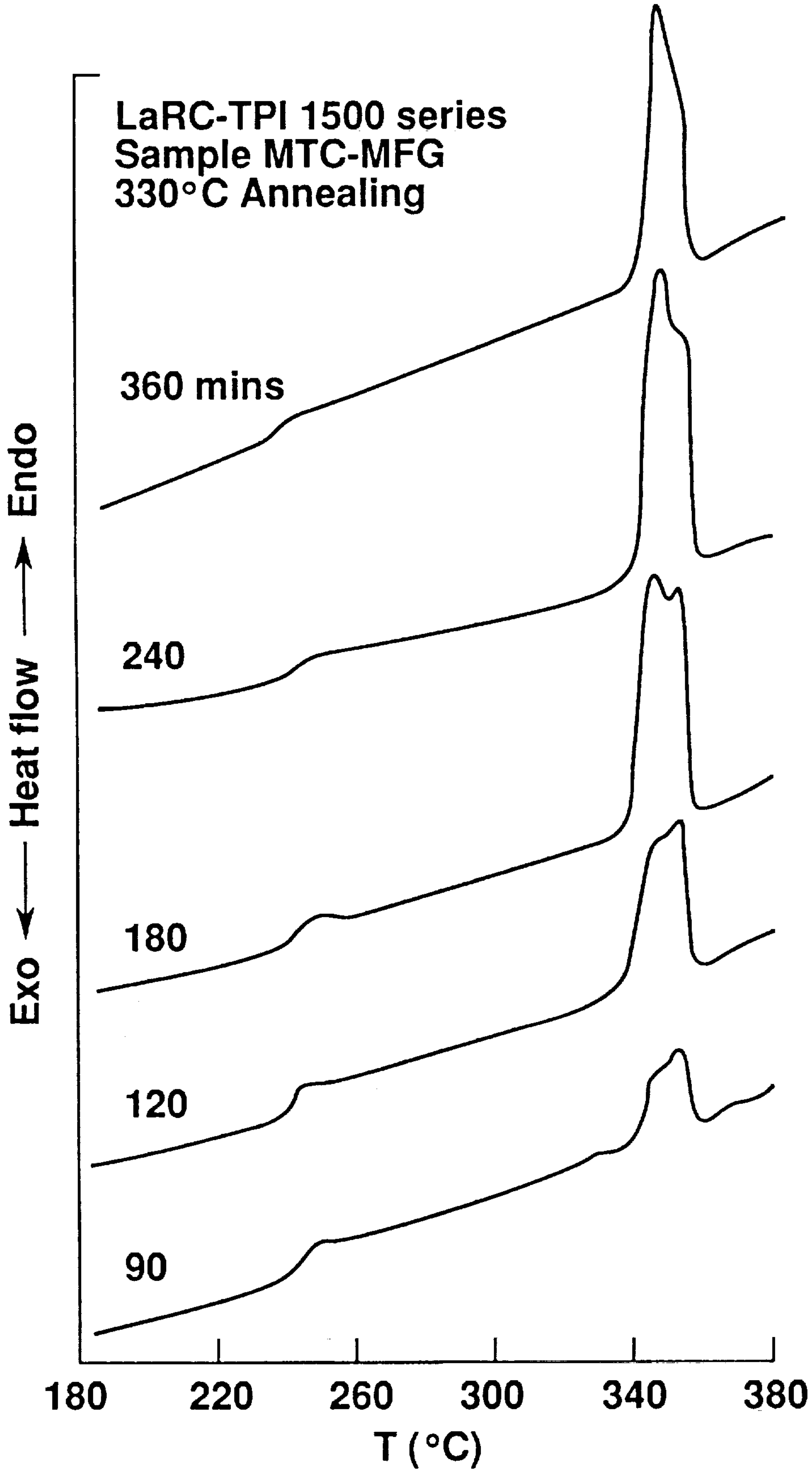

Figure 5. DSC thermograms for the MTC-MFG polymer annealed at 330°C for various lengths of time indicated.

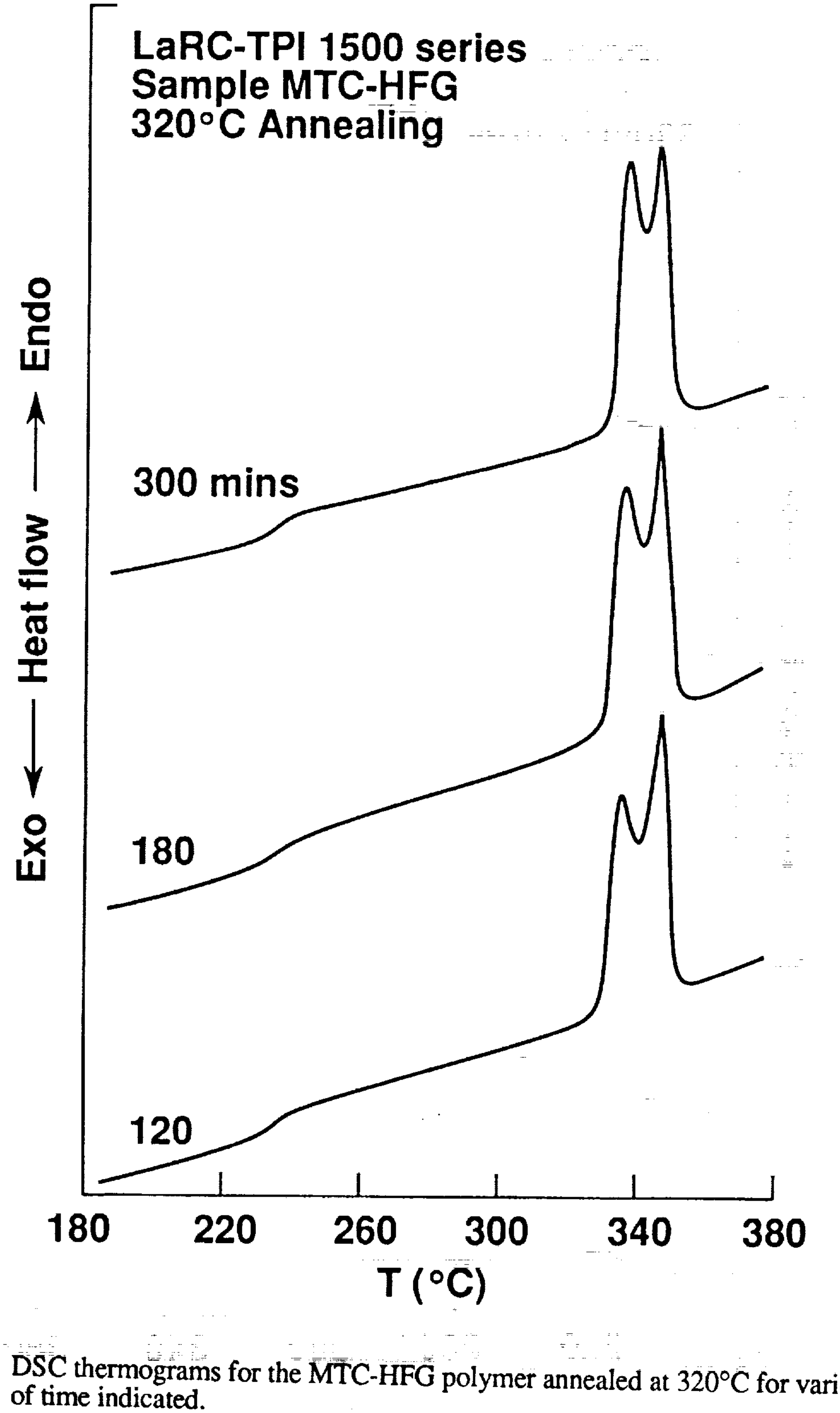

Figure 6. DSC thermograms for the MTC-HFG polymer annealed at 320°C for various lengths of time indicated.

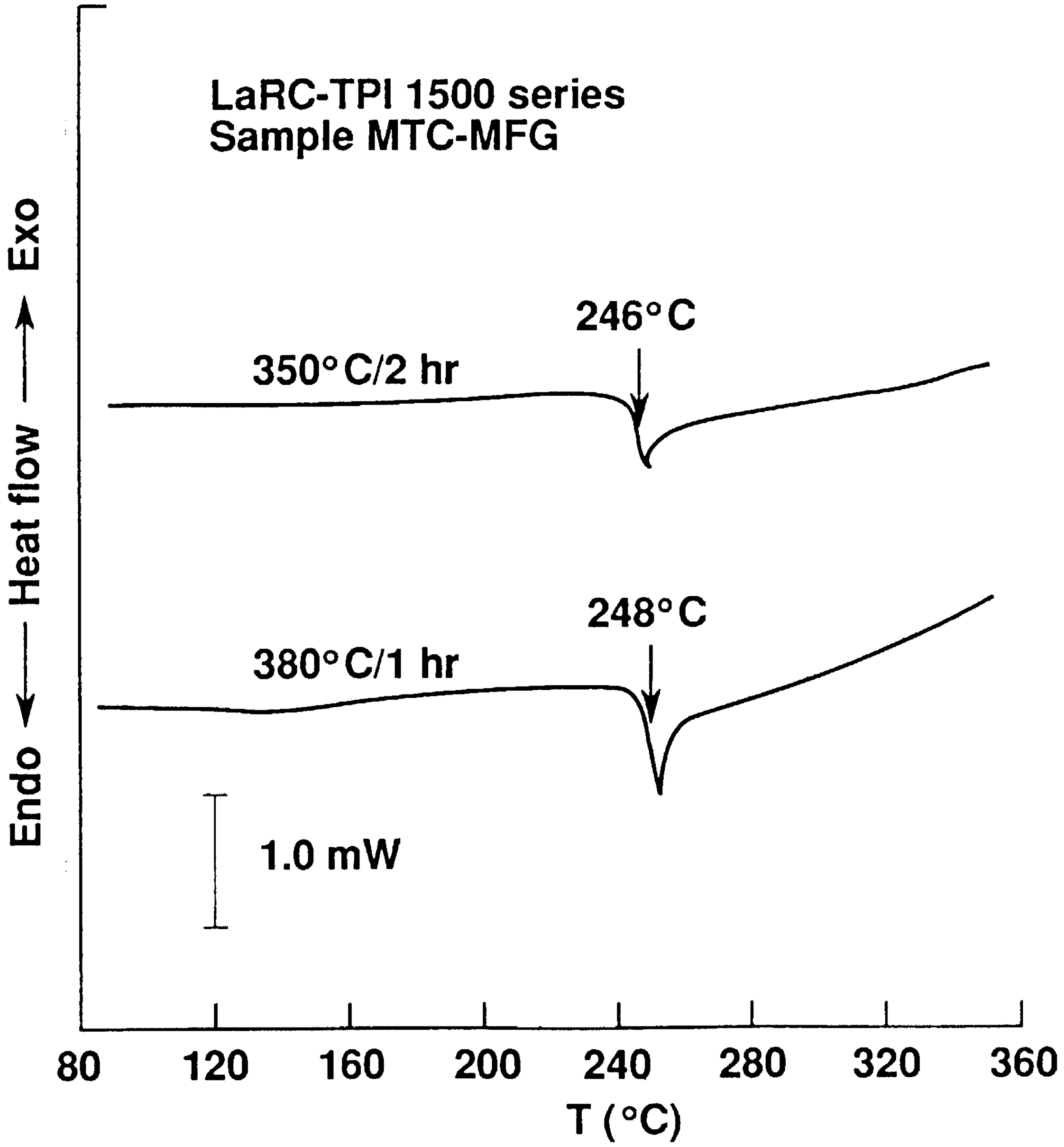

Figure 7. DSC thermograms for the MTC-MFG samples annealed under the conditions of 350°C for 2 hrs. and 380°C for 1 hr., respectively.

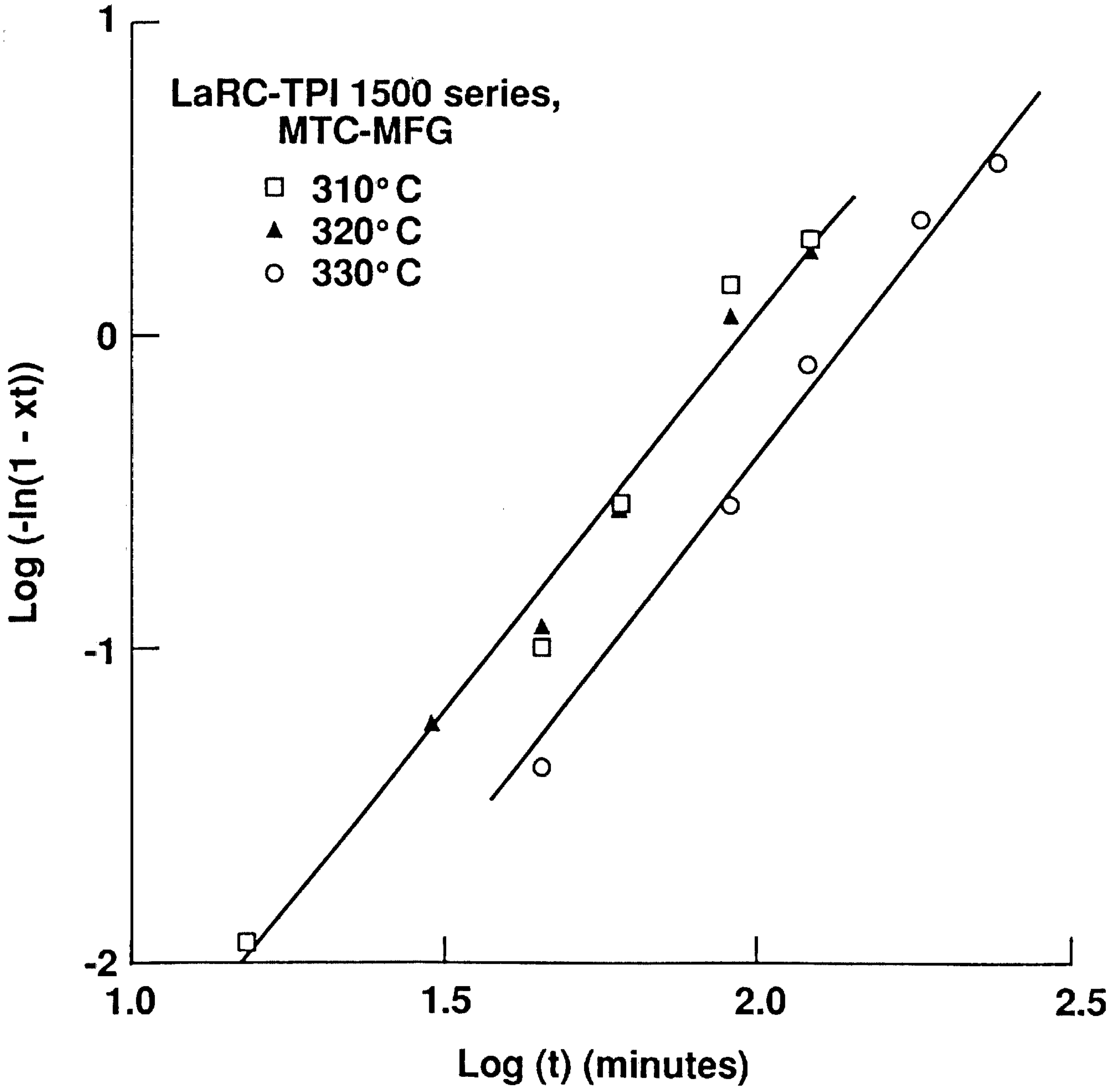

Figure 8. Linear plot of the Avrami Equation (Eq. (2)) for the study of the crystallization kinetics of MTC-MFG polymer.

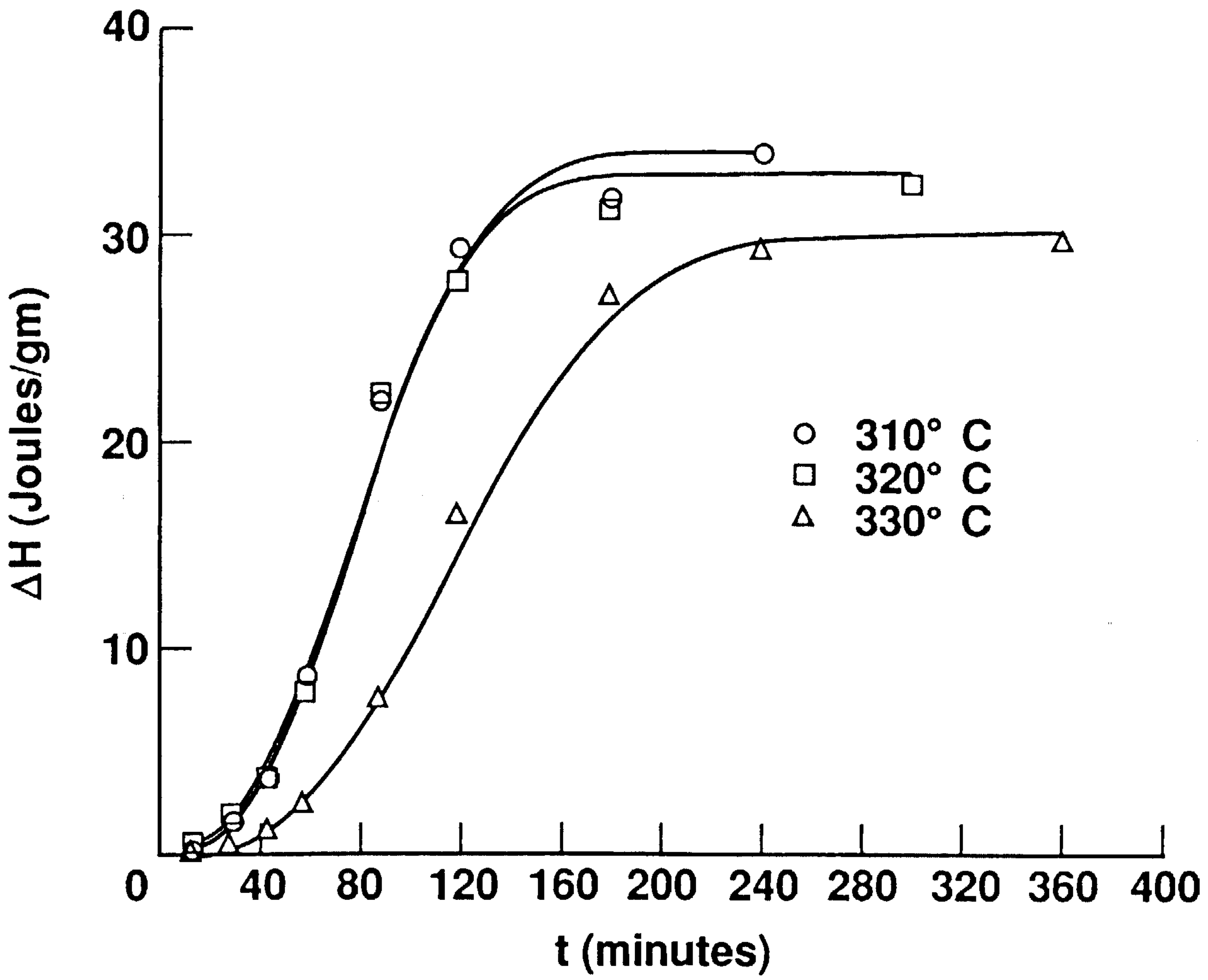

Figure 9. Comparison of the experimental data (symbols) and the Avrami Equation (Eq. (1)) predictions (lines)

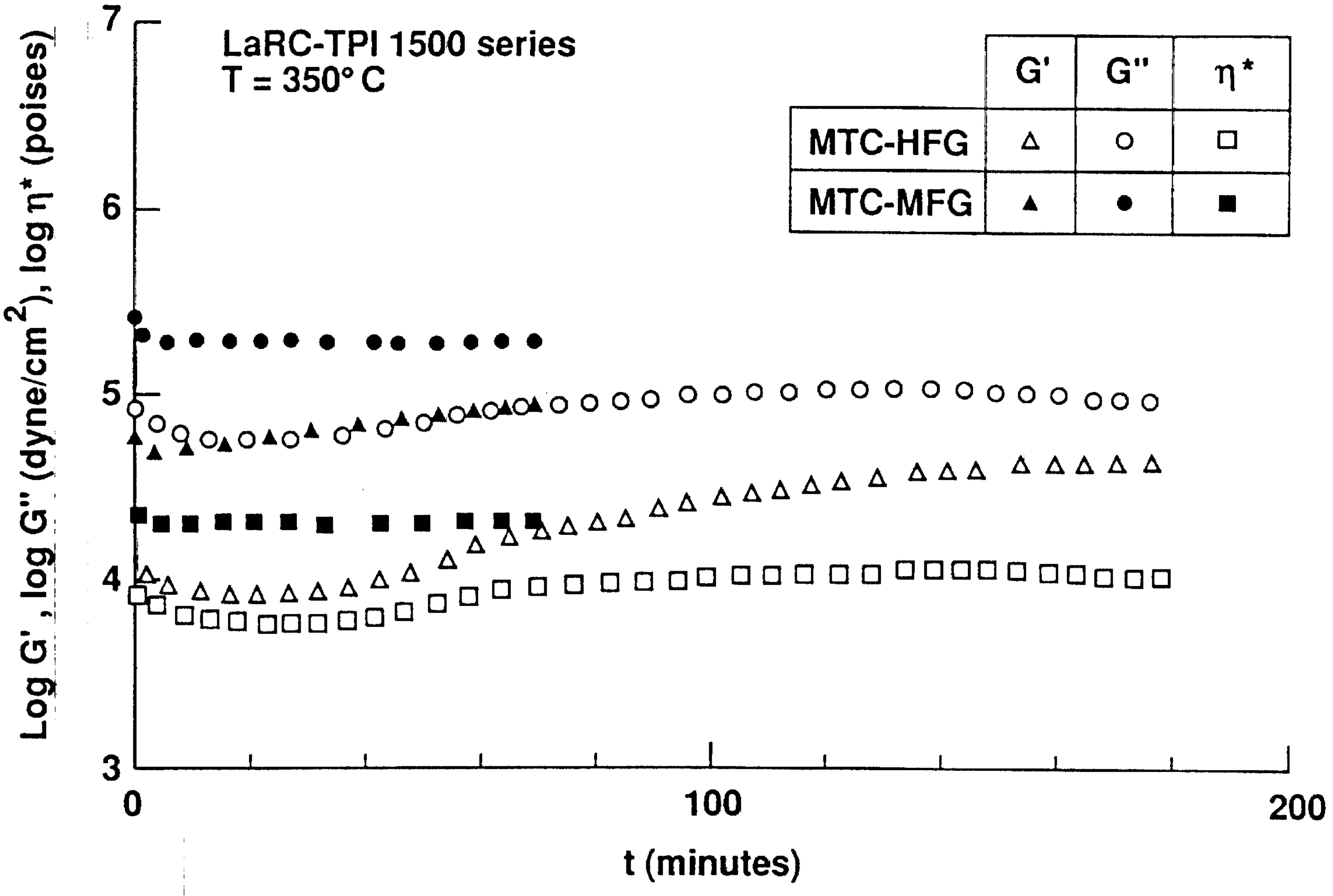

Figure 10. Thermal stabilities of the viscoelastic properties of the MTC-HFG and the MTC-MFG polymers at 350°C .

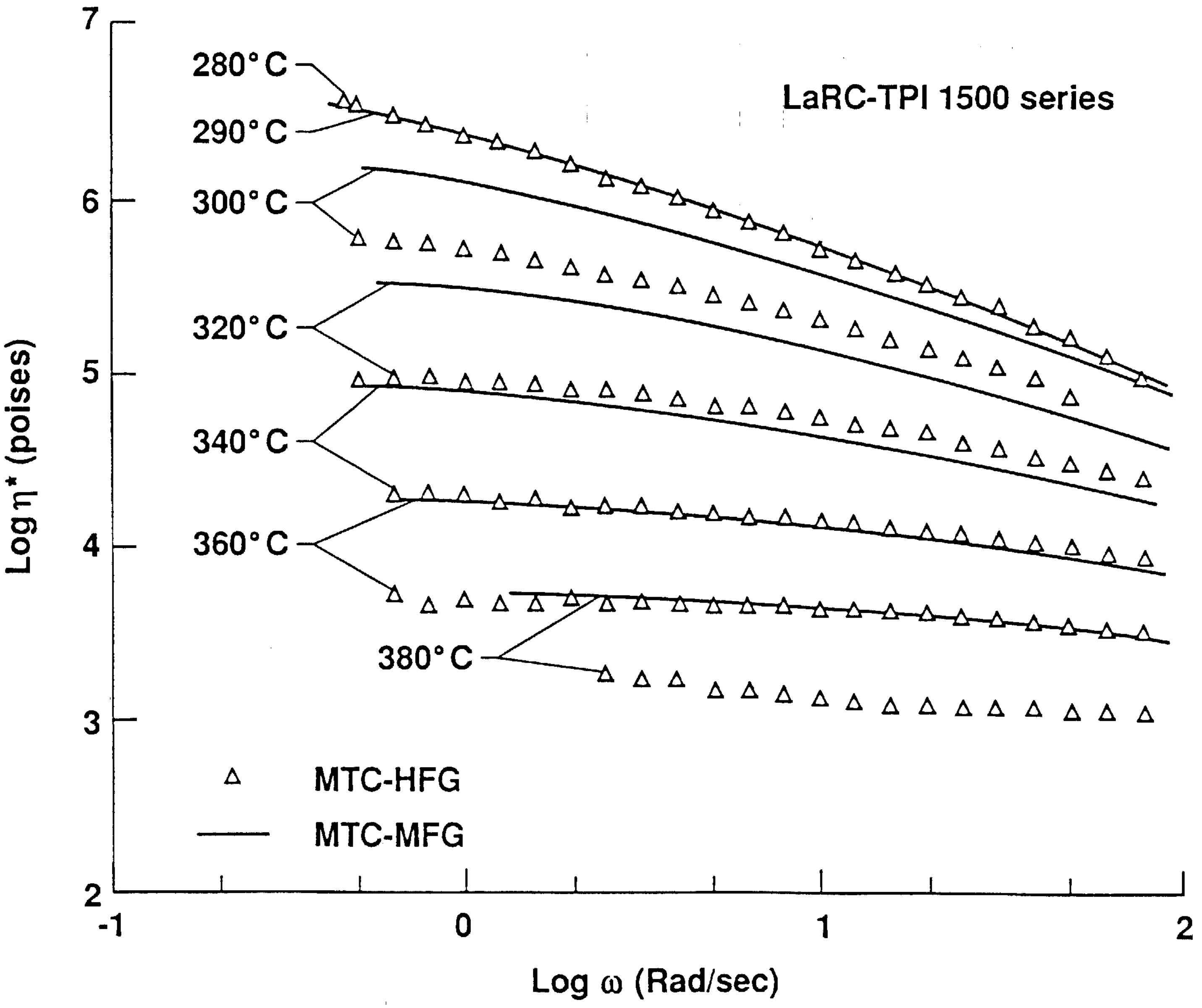

Figure 11. Complex viscosities of the MTC-MFG and the MTC-HFG polymers measured at various temperatures indicated.

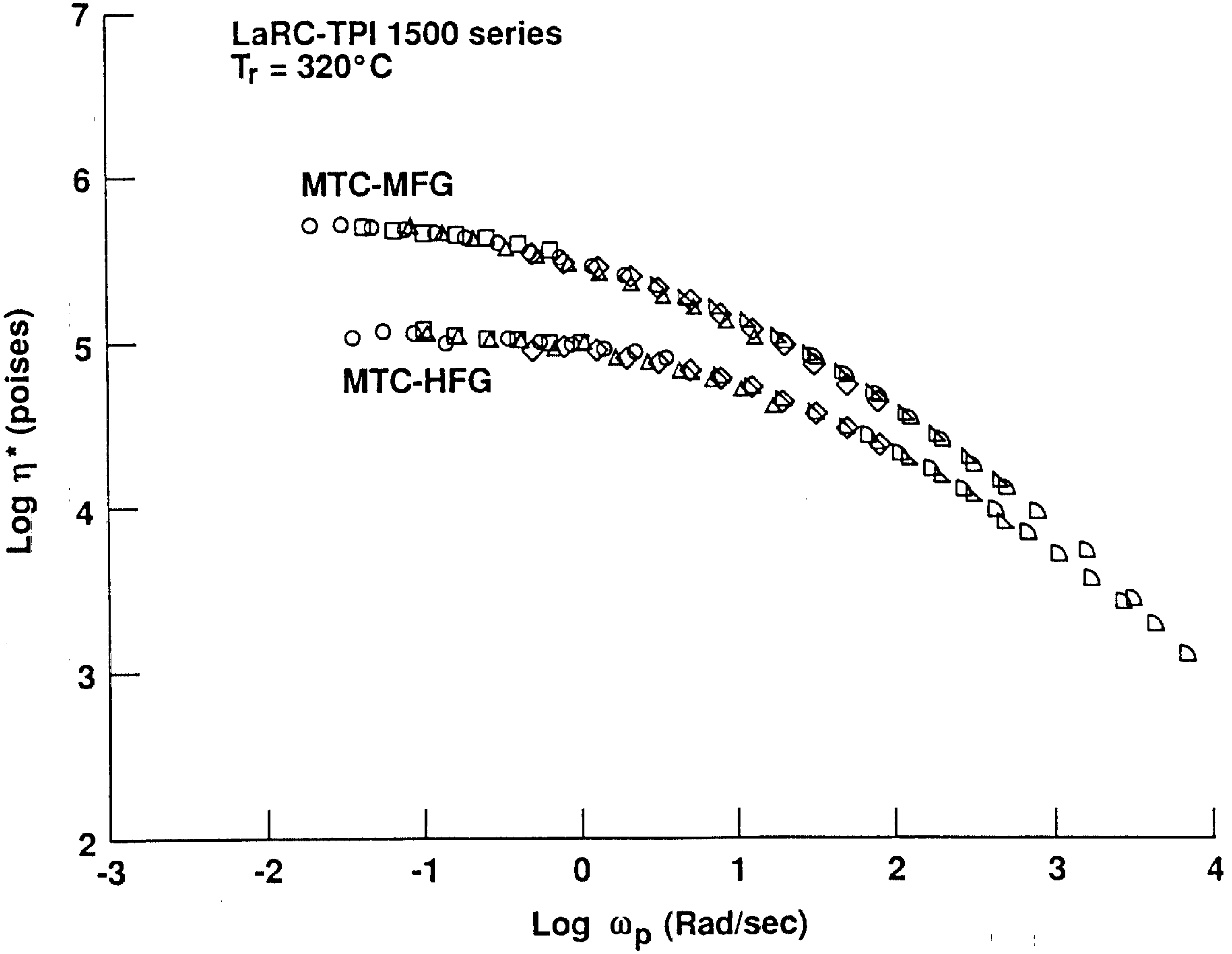

Figure 12. Master curves of the complex viscosities at 320°C for the MTC-MFG and the MTC-HFG polymers, respectively.

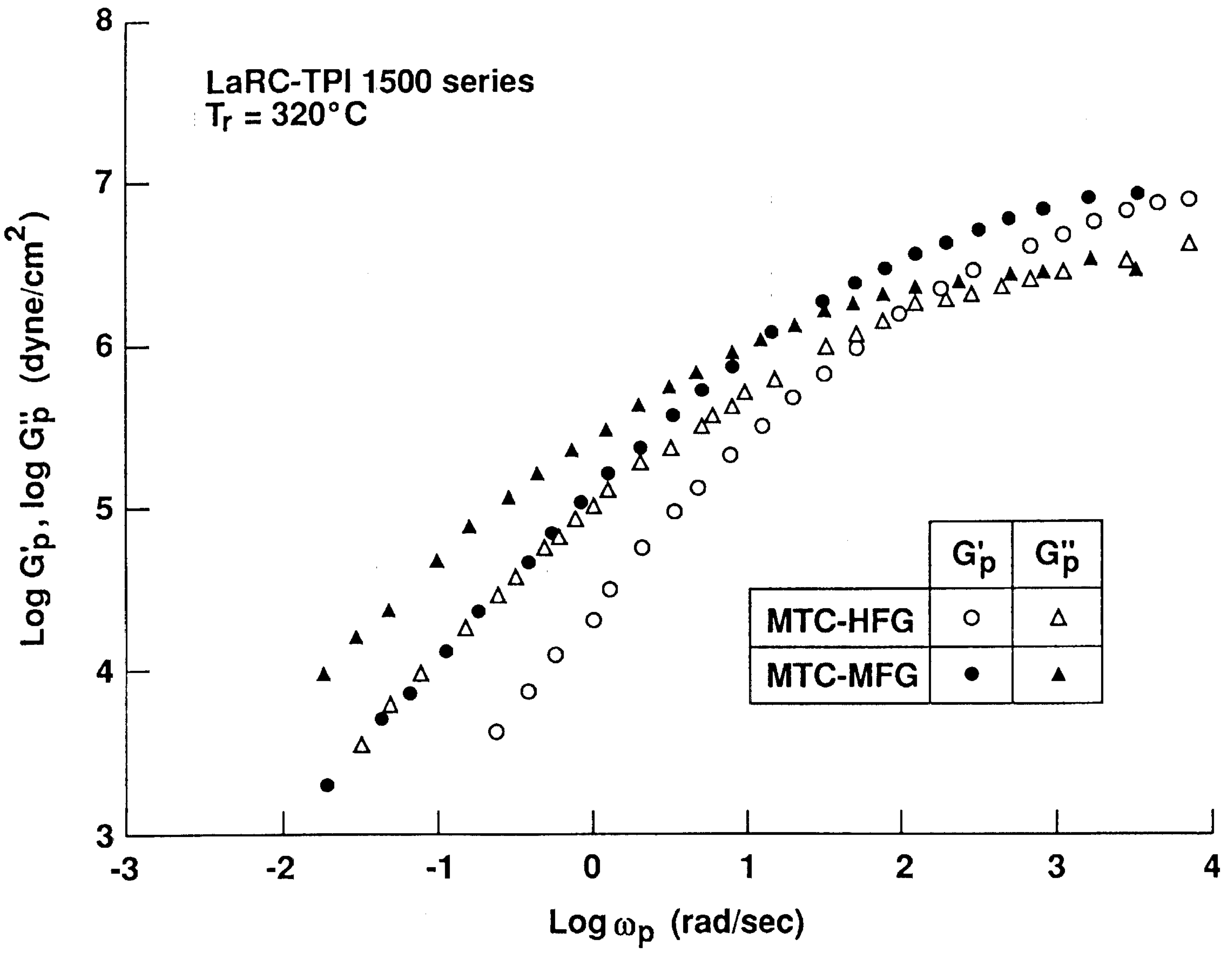

Figure 13. Master curves of the storage (G_p') and the loss (G_p") moduli at 320°C for the MTC-MFG and the MTC-HFG polymers, respectively.

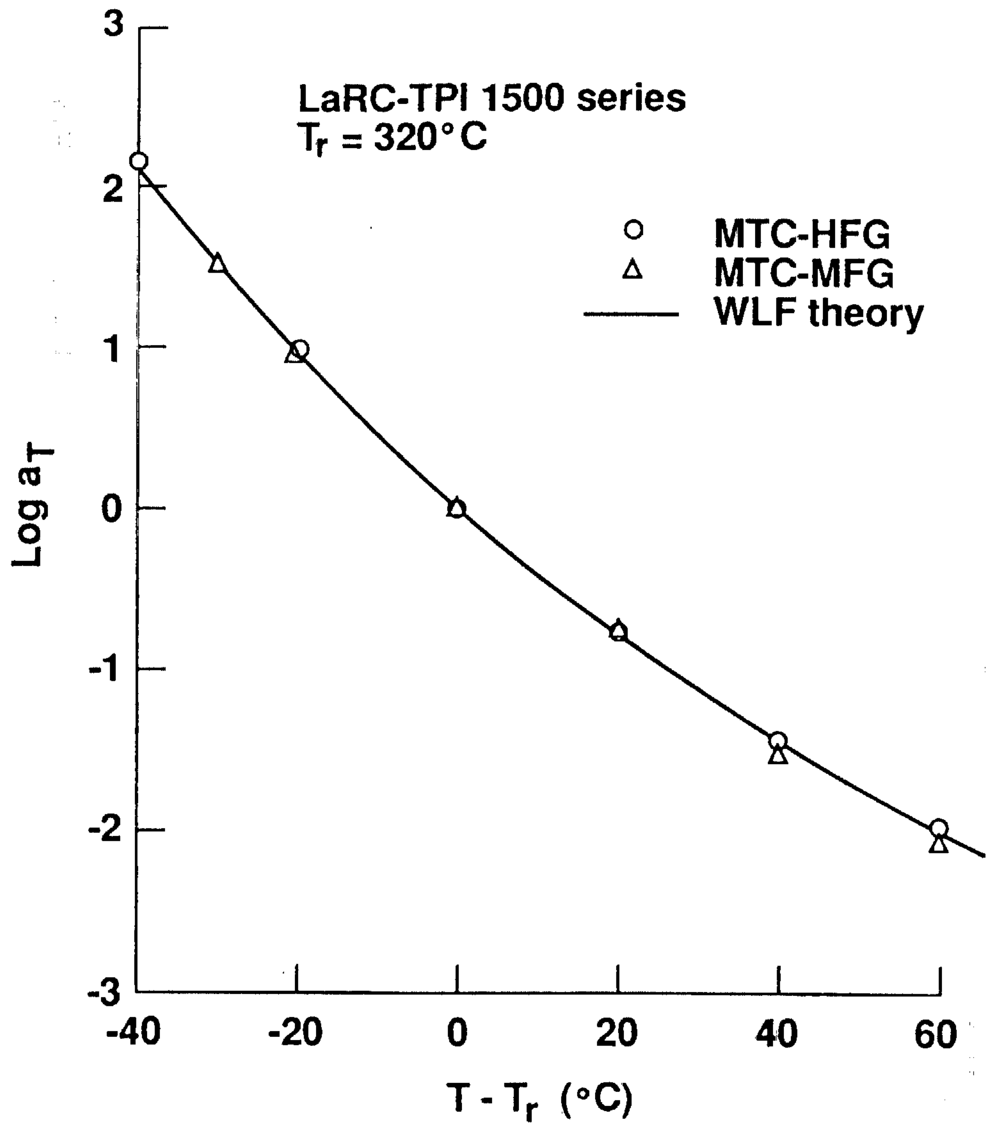

Figure 14. Comparison of the shift factors and the WLF theory for the MTC-HFG and the MTC-MFG polymers.

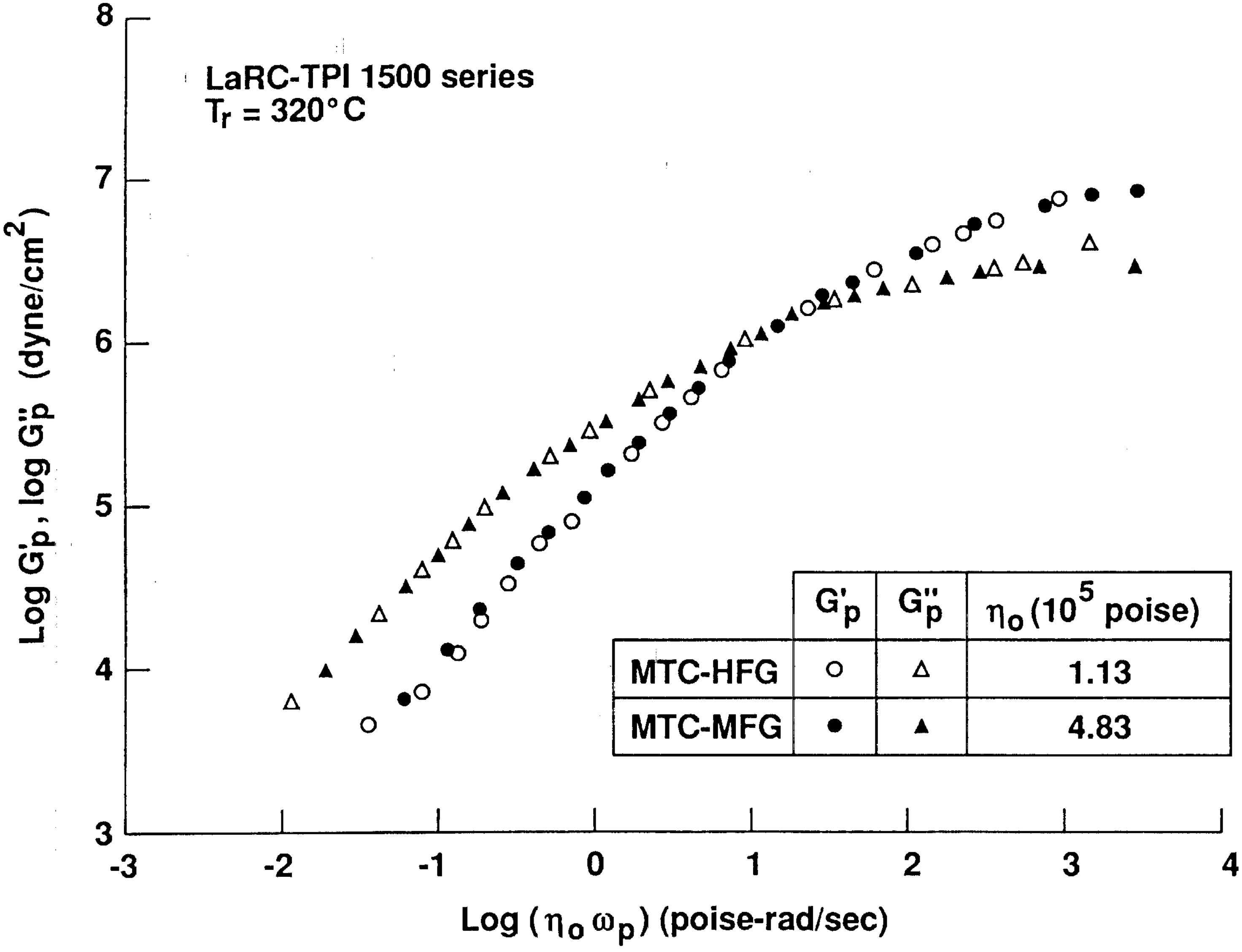

Figure 15. Plots of the master curves of G_p' and G_p'' vs. the reduced frequency $\omega_R = \eta_o \omega_p$ as suggested by Zeichner et al.[22].

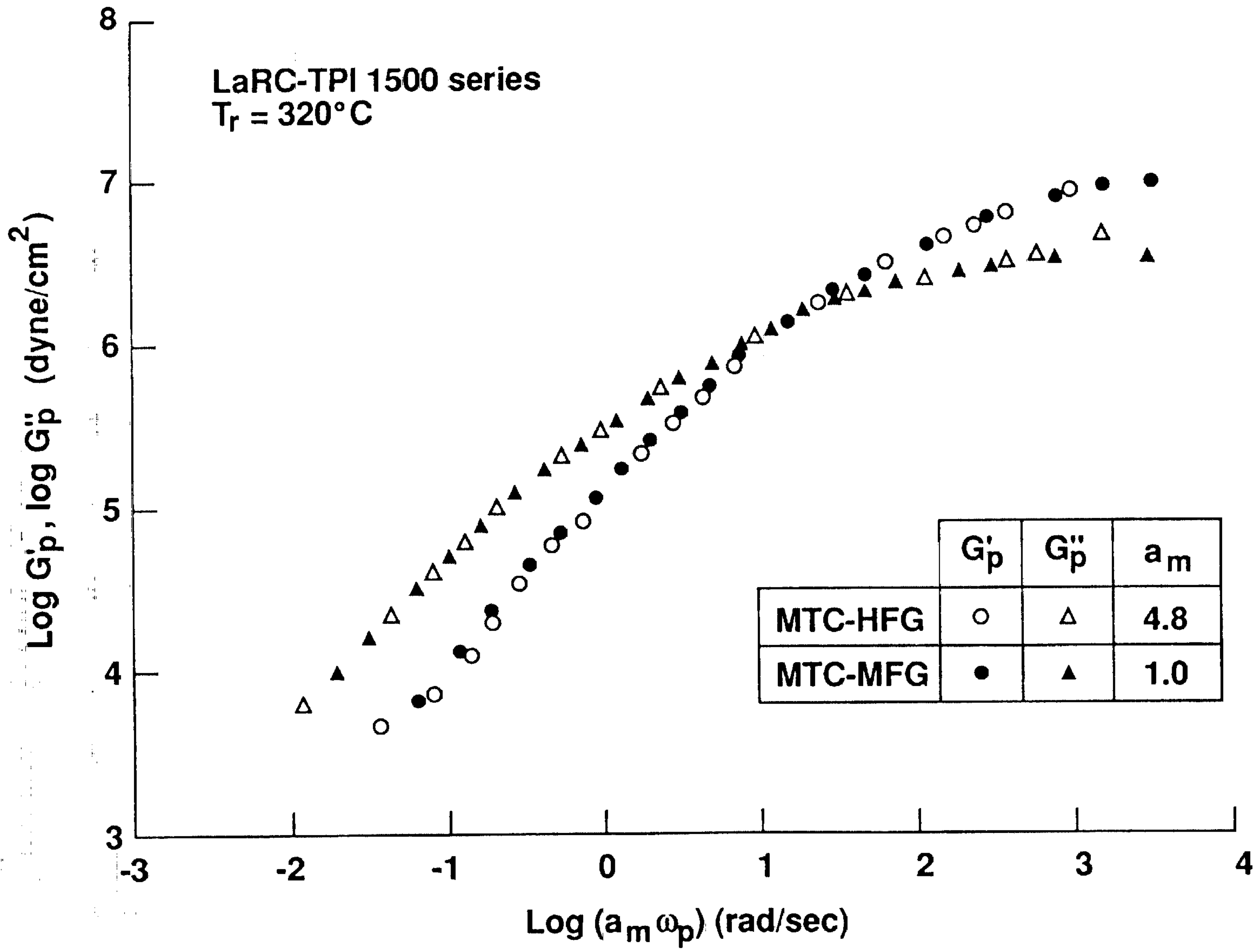

Figure 16. Plots of the master curves of G_p' and G_p'' vs. the reduced frequency $\omega_R = a_m \omega_p$ as suggested by Dormier et al.[23].

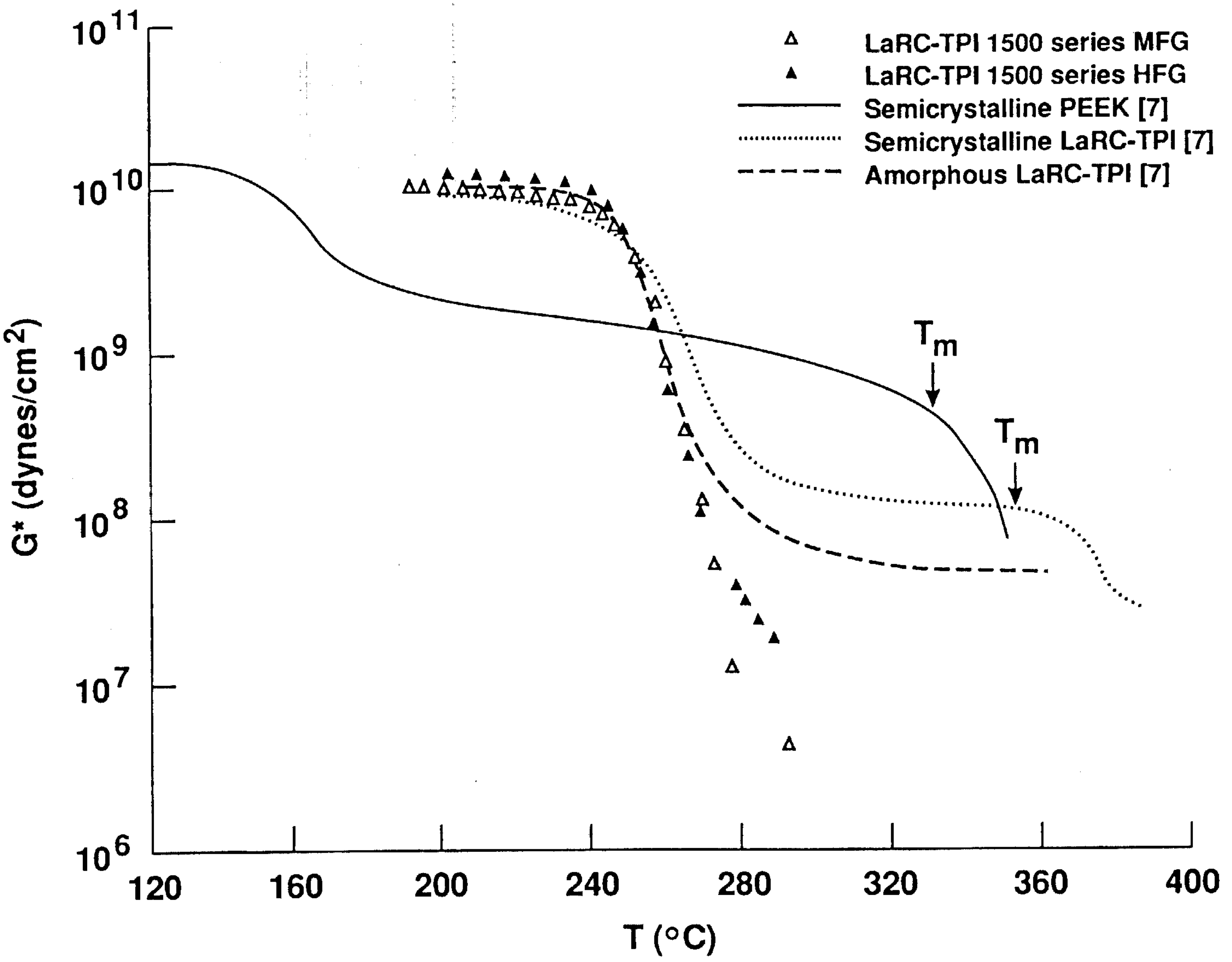

Figure 17. Complex moduli as a function of temperature for various polymer samples.

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Final Report

16. Abstract

The crystallization behavior and the melt flow properties of two batches of 1500 series LaRC-TPI polymers from Mitsui Toatsu Chemicals (MTC) have been investigated. The characterization methods include Differential Scanning Calorimetry, the X-ray diffractography and the melt rheology. The as-received materials possess initial crystalline melting peak temperatures of 295 and 305°C, respectively. These materials are less readily recrystallizable at elevated temperatures when compared to other semicrystalline thermoplastics. For the samples annealed at temperatures below 330°C, a semicrystalline polymer can be obtained. On the other hand, a purely amorphous structure is realized in the samples annealed at temperatures above 330°C. Isothermal crystallization kinetics were studied by means of the simple Avrami equation. The viscoelastic properties at elevated temperatures below and above T_gs of the polymers were measured. Information with regard to the molecule sizes and distributions in these polymers were also extracted from melt rheology.

17. Key Words (Suggested by Author(s))
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