Chapter 3

Semi-Flexible Semicrystalline Polyimides- Literature Review

3.1 Introduction

The prime objective of this research is to develop and characterize high temperature and high performance thermoplastic semicrystalline polyimides. Although strong arguments for such a research project would be presented in the proposal section of this report, this section will focus on the literature review of studies on this class of materials. The following section reviews the work in this area from the perspective of goals for this study. In this regard, this review will first focus on the crystallization ability of the various semicrystalline polyimides reported in literature. A special focus will be on the ability of these materials to crystallize from the melt. Thermal stability of various polyimides, with respect to the recrystallization from various melt conditions will be discussed. The review will also address the morphology of these systems and both microscopic and SAXS information will be reviewed. Crystallization kinetics of such melt processable polymers is extremely important from both a practical and fundamental standpoint and results in the literature will be discussed in this regard. Another important feature frequently exhibited by these polymers is the multiple melting behavior. The possible explanations of this phenomenon put forward in the literature will be highlighted. Lastly, results dealing with rheological and physical properties of this class of materials will be reviewed.
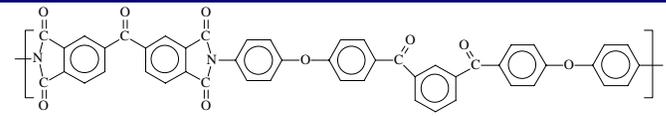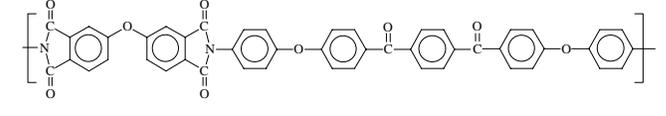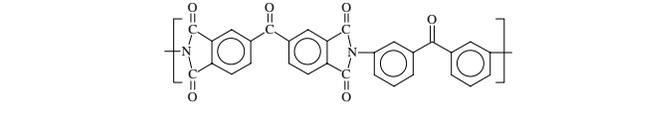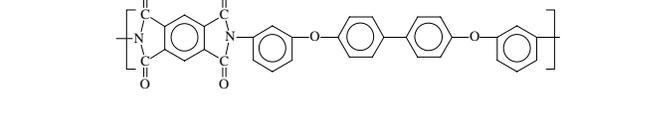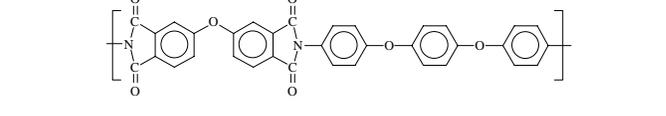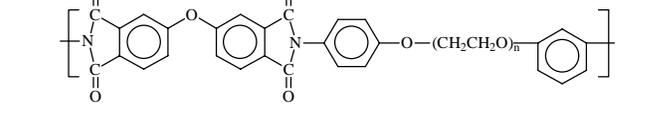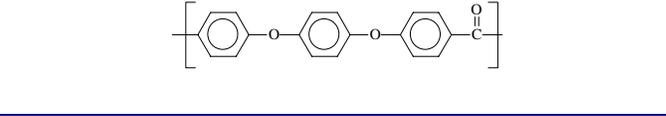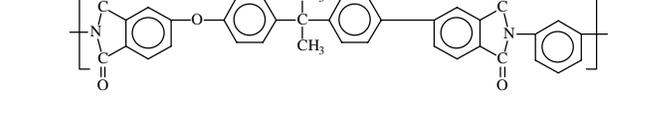
3.2 Crystallization behavior from the melt

Although many crystalline polyimides have been reported in literature[1,2,3,4,5,6], the studies dealing with melt crystallization of these systems are scarce. As discussed in Chapter 1, polyimides with the appropriate chain structure will crystallize during the imidization process. It is however important to recognize that imidization of poly (amic acids) takes place in the presence of polar aprotic solvents and thus the initial processes of imidization and crystallization take place simultaneously. The initial crystallization is thus solvent aided and starts taking place before the chain attains its full rigidity. For crystallization from the melt however, the inherent crystallizability of the semi-flexible chain itself is important. Most initially semicrystalline polyimides lack this inherent crystallizability. The second important factor is the very high melting point (>350°C) usually associated with such systems. At these temperatures, the possibility of degradation reactions leads to material being susceptible to crosslinking, chain scission and branching reactions. These degradation mechanisms, if they occur, will also lead to decreasing recrystallization ability. Of the several such systems discovered, New-TPI[7,8,9] (New-Thermoplastic Polyimide) originally developed and licensed by Mitsui Toatsu Chemicals, has probably been the most popular system in attracting the attention of several research groups[10,11,12,13]. Before New-TPI though, several other systems which showed varying degree of promise were developed by workers at NASA, many of them later being characterized in this laboratory. These were LaRC-CPI[3,14,15] (Langley research center-crystalline polyimide), LaRC-CPI-2[16,17] (second generation) and LaRC-TPI[18]. Another system investigated in this laboratory later was TPEQ-ODPA[19]. The structures of these polyimides and their glass transitions and melting points are shown in Table 3.1[3,7,16,19,4]. It is important to mention that for each of these polyimides, there were several different grades that essentially differed in their molecular weight or sometimes the nature of the endcapping. The crystallizability of the different grades is different.

Most of these polyimides display the essential characteristics of T_g (>200°C) and high T_m's (>350°C) and thus are candidates for high temperature and high performance applications from this standpoint. The desired recrystallization ability from the melt of these materials, however,` is not like a typical thermoplastic. Figure 3.1 shows the

second heat DSC scans for different grades of LaRC-CPI[3] after quenching from the melt. The lowest molecular weight 'A' is the only version showing the ability to crystallize after having been taken once to melt conditions. It is clear that the higher molecular grade labeled 'B' shows a much more sluggish crystallization behavior with the highest molecular weight versions (C&D) showing no crystallization ability. Similar behavior is also observed for LaRC-CPI-2[16] in Figure 3.1 (first heat scans) which shows that higher molecular weight samples (lower offset) show significantly decreased ability to crystallize. LaRC-CPI-2[16] also exhibits dual melting behavior with additional annealing being necessary to eliminate the lower melting form. While lower molecular weights increase the crystallization ability to some extent, they also lead to poorer mechanical properties (LaRC-CPI-2 films also show low elongation to break of less than 5%).

Figure 3.1 shows the first heat scans and subsequent heating scans at different heating rates for the TPEQ-ODPA[19] polyimide. While the polymer exhibits crystallinity in the initial sample, the recrystallization ability decreases markedly once the polymer is taken to melt. Slower heating rates only seem to have a limited impact in improving the crystallinity and longer annealing times are required to induce crystallinity in the material. From the crystallization ability viewpoint, a superior behavior is exhibited by New-TPI[9], probably the only semicrystalline polyimide successful in achieving wide attention from different academic and industrial research groups and also successfully commercial today. Figure 3.2 shows the second heat DSC scans for both a higher molecular weight (HV) and lower molecular weight (LV) versions[9] after quenching from melt conditions. Both versions show stability of the melting point although the amount of crystallinity decreases substantially for the higher molecular weight version after the first heat. The lower molecular weight version seems to show slower crystallization kinetics from the melt with a significant crystallization occurring only during the heating scan from the room temperature. Also, for the lower viscosity samples it was found that isothermal crystallization at temperatures lower than 350°C was successful in inducing crystallinity and thus eliminated crystallization exotherms during heating.

Table 3.1   Chemical structures and T_g's and T_m's of various semicrystalline polyimides. The structures and values for ULTEM, an amorphous polyetherimide, and PEEK are also shown.

Chemical Structure	Name	T_g(°C)	T_m(°C)
	LaRC-CPI	220	360
	LaRC-CPI-2	217	334 & 364
	LaRC-TPI	240	330-350
	New-TPI	250	385
	TPEQ-OPDA	238	420
	Ethylene Glycol based diamine-ODPA	112 n=3 145 n=2 177 n=1	268 n=3 304 n=2 340 n=1
	PEEK	143	334
	Ultem®-PEI	215	ND
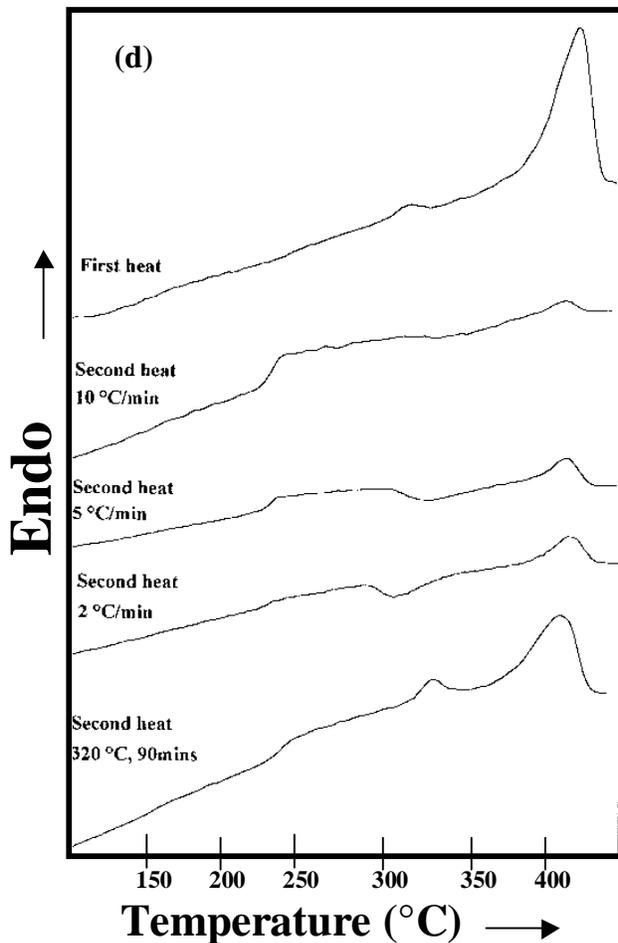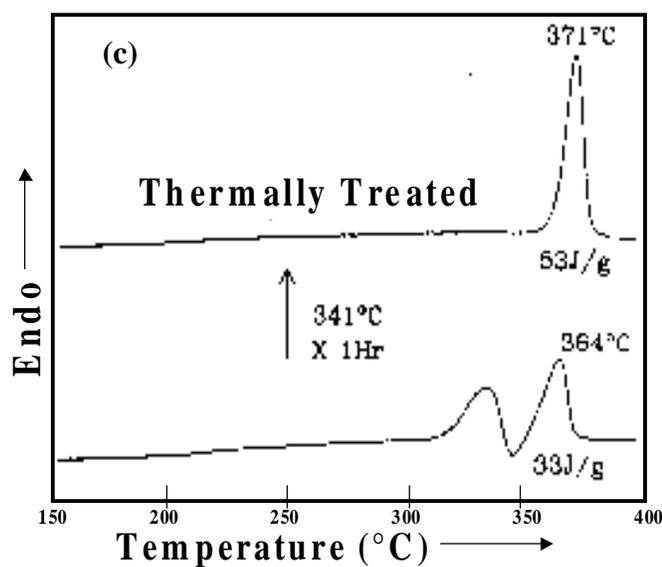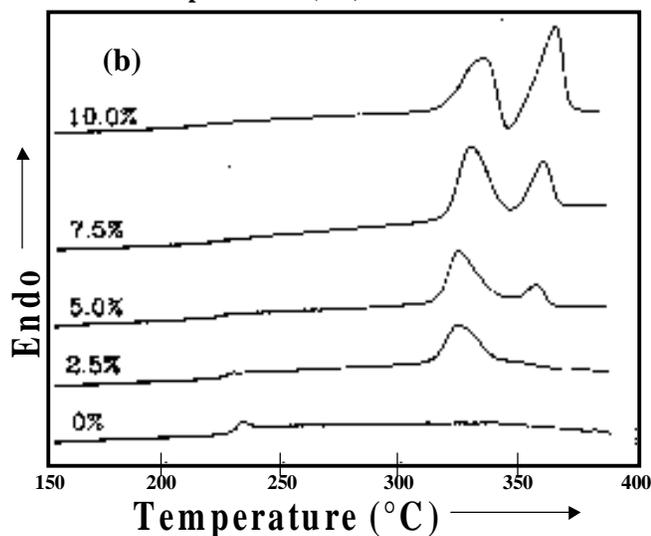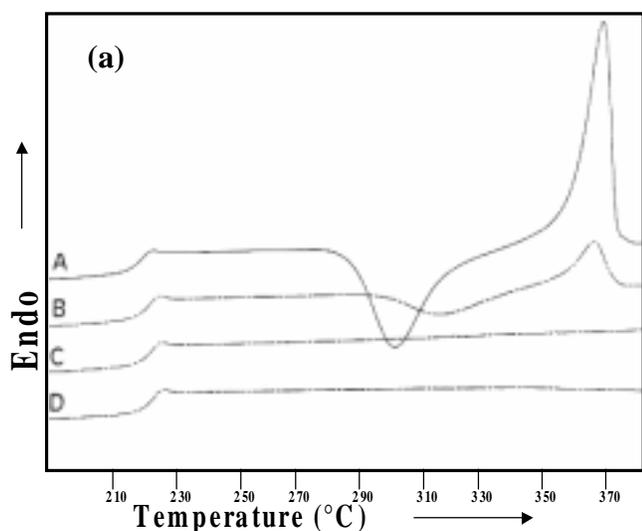
Figure 3.1 (a) Second heat DSC scans of LaRC-CPI after having been previously taken to melt and quenching. While A is the low molecular weight version, others are increasingly of higher mol. wt.[3] (b) First heat DSC scans of variously stoichiometrically offset LaRC-CPI-2 polyimide films.[16] (c) DSC scans of LaRC-CPI-2 films showing changing melting behavior after annealing treatment. (d) First and consecutive heating scans for TPEQ-ODPA polyimide showing sluggish crystallization behavior[19].

While these results were promising, work conducted at different melt temperatures and times better characterized the window available in the melt from which the material could be crystallized without appreciable loss in degree of crystallinity. Unfortunately these results are not very exciting and show only a very limited thermal stability in the melt. Figure 3.3 illustrates the results for a range of melt times and temperatures with each point in the grid representing an individual DSC scan[20]. Longer times and temperatures in the melt lead to a big drop in the crystallizability. The material seems to show significant drop in the heat of melting if melt residence times are longer than 10 minutes. From the practical standpoint, these results are disappointing and limit the range of melt operations that can be carried out.

3.3 Crystallization Kinetics

Fast crystallization kinetics from the melt becomes a crucial factor when these systems are processed from the melt. A faster crystallization response is obviously favorable from an economical perspective as it leads to decreased cycle times. A slower crystallization rate may force additional annealing times at certain temperatures and may in fact become a rate-determining step. In this regard, the traditional Avrami analysis has been utilized to quantify the bulk crystallization kinetics for some semicrystalline polyimides. Using this analysis for LaRC-CPI[3], Muellerleile et al. found that the value of Avrami exponent was ca. 2 and surprisingly this value did not show much change with varying T_c. Morphological investigations revealed the existence of hedritic or sheaf-like structures, which gave additional credence to the values of Avrami exponent obtained. The value of bulk crystallization rate 'K' however could not be calculated reliably which therefore precludes any reliable comparisons with other systems. The thermal behavior for this polyimide indicated in Figure 3.3, and other DSC results presented by the authors, however, indicate only a sluggish crystallization response and limited thermal
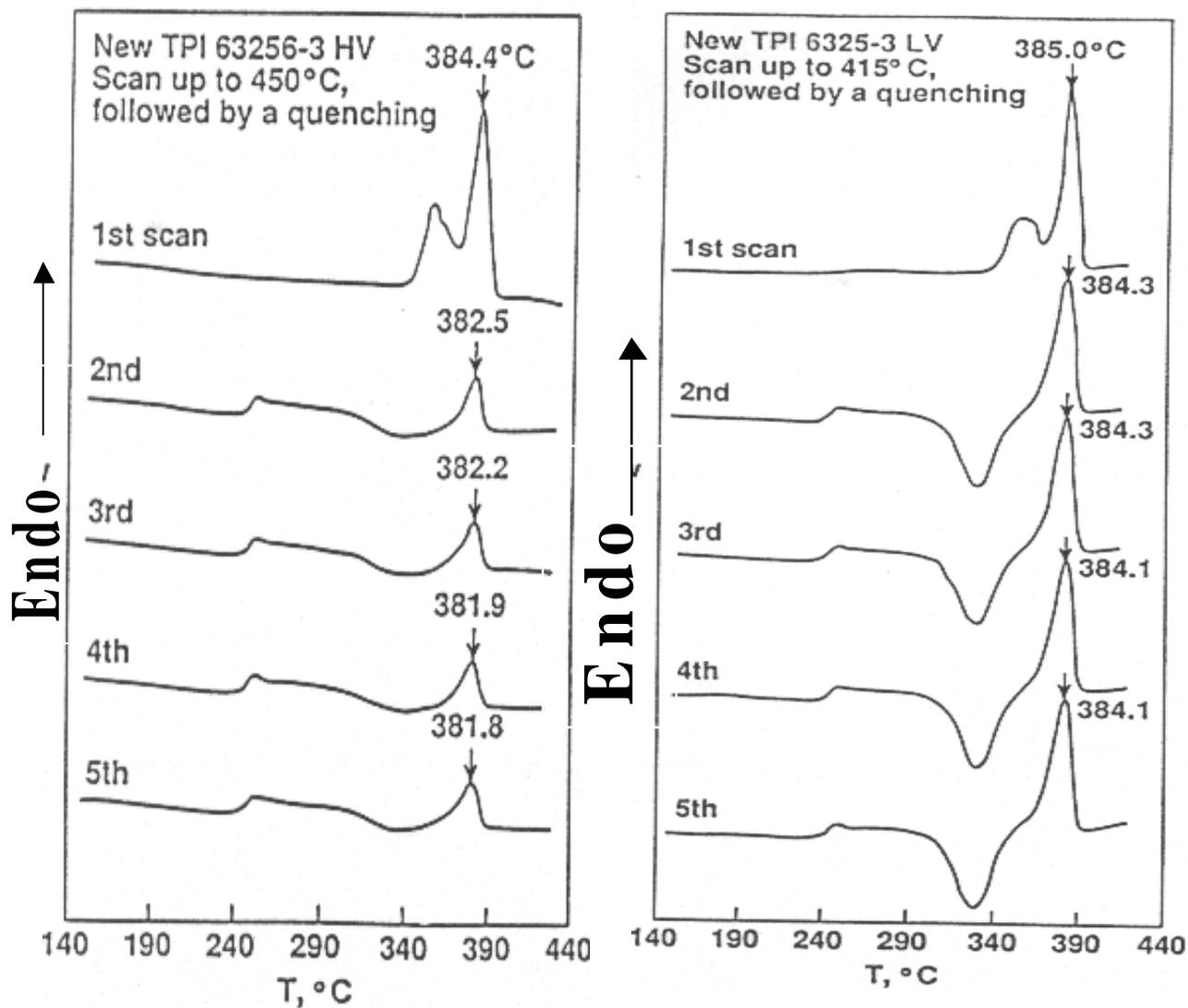
Figure 3.2 First heat and repeat heat DSC scans for the commercial New-TPI[9]. The scans are shown for two different grades (a) High Viscosity grade (b) Low viscosity grade.
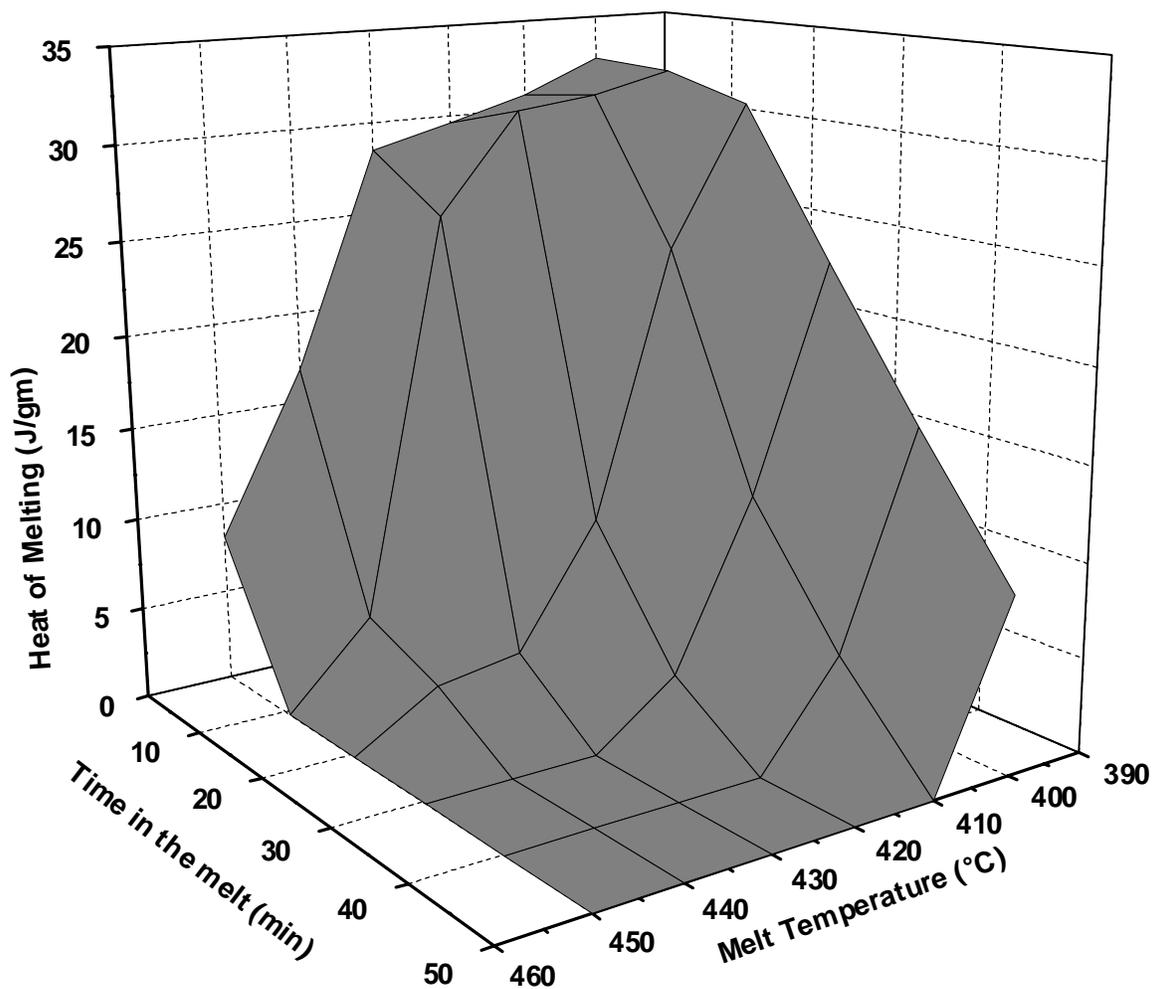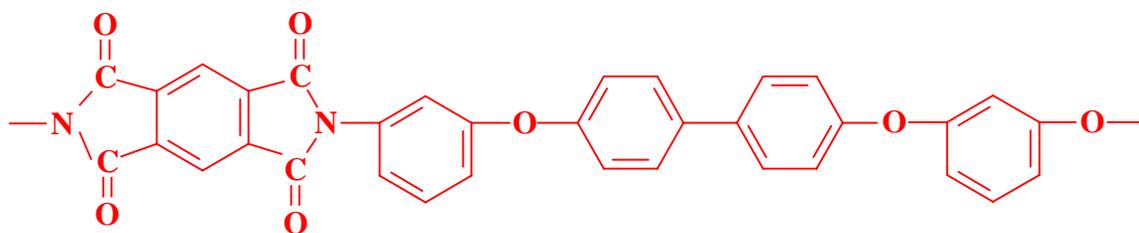
Aurum New-TPI

Figure 3.3   Chemical structure and thermal stability of New-TPI polyimide. The 3-D plot illustrates the heat of melting after exposures to different melt temperatures and melt residence times[20].

stability in the melt. For LaRC-CPI-2, attempts by Brandom[16] to perform Avrami analysis failed (by DSC) as a suitable exothermic signal could not be obtained for a range of melt conditions. While milder melt conditions led to a crystallization exotherm starting before the stabilization of the DSC signal, other more harsher conditions produced only a very weak exotherm. The authors thus observed faster response only in a narrow range of undercoolings and when using only very mild melt conditions. This behavior and other similar results presented in the study is due to incomplete melting (memory effect) and presence of large amounts residual nuclei, which then aid in subsequent crystallization. Once higher melt temperatures/times were utilized and these residual nuclei were destroyed, *the lack of inherent crystallizability* of the chain led to only a sluggish and weak crystallization response. Other attempts to quantify the crystallization behavior of LaRC-CPI-2 by Brandom[21] involved using rheological measurements to perform Avrami analysis. The results indicated very high values of 'n' and 'K' and do not lend themselves to a conclusive interpretation. Additionally, the utilization of Avrami analysis (see Chapter 2) on rheological data, where the sensitivity is limited to the onset of crystallization, and the complete primary crystallization process cannot be followed reliably, is a very controversial proposition. For a different polyimide TPEQ-ODPA[22], characterized in this laboratory by Srinivas et al.[19,22], the crystallization kinetics is again very slow. Three molecular weight versions were tried and only the low molecular weight version of M_n=10,000 Daltons resulted in any significant crystallizability. For this polyimide and others possessing similar structure, it has been observed that such low molecular weights result in very brittle films. However, M_n of 15,000 Daltons or more often leads to creasable films. It is thus likely that molecular weight of M_n=10,000 Daltons is either close to or below the critical molecular weight for entanglements and hence properties of the initial film are very poor. For TPEQ-ODPA, higher molecular weight versions showed a much reduced chain mobility and crystallized appreciably only in the presence of NMP. The very slow crystallization response and overall a languid crystallization behavior did not make any isothermal crystallization kinetics viable in this case. The story regarding the crystallization kinetics for another semicrystalline NASA polyimide LaRC-TPI, is yet again grim due to poor recrystallization stability from the melt[23]. Two separate attempts at performing Avrami

analysis have been made by NASA workers[18] and by Muellerleile[24] in this laboratory. NASA workers found the Avrami exponent to be '1' and ca. '2.5' for two different grades of LaRC-TPI. The value of the bulk crystallization rate parameter 'K' was found to be very low (at T_c of 280°C), the exact value being very unreliable and hence not being reported here. For New-TPI the crystallizability and crystallization rates are significantly better compared to the polyimides discussed above. Before presenting the absolute value of 'n & K' it is useful to recall from Chapter 2 that the value and units of K are dependent on value of n. Hence to make valid comparisons, values of $K^{1/n}$ should be compared. Secondly, the undercooling at which the crystallization is carried out will have a major influence. The values of 'n & $K^{1/n}$' that were found by Hsiao et al[25]. are 4 and 0.04 min^{-1} for thermal nucleation and the fastest rate observed. In this regard, it is useful to compare results with PEEK which, though not a polyimide, competes with polyimides in a variety of applications. Cebe and Hong[26] have reported a value of 0.22 min^{-1} for $K^{1/n}$ at an undercooling of 87°C. Although the highest value of $K^{1/n}$ is reported here, it will be subsequently discussed in this research that value of $K^{1/n}$ is critically dependent on the previous melt conditions. Also, the results presented later for the polyimide researched in this work will show the rates of crystallization to be faster by more than a decade than the values shown above. It also needs to be mentioned that for many of these rigid polymer systems, equilibrium melting points are not known with certainty. Hoffman-Weeks analysis which has often been utilized for such a purpose is strictly inapplicable for estimating equilibrium melting points of these polymers. Thus there is some degree of inaccuracy when describing the exact undercooling at a given crystallization temperature. This could in turn sometimes lead to erroneous comparisons of crystallization kinetics for two polymers at the same stated undercooling.

3.4 *Morphology of Semicrystalline Polyimides*

Despite increased overall chain-rigidity and a highly aromatic backbone, these high temperature semicrystalline polyimides (at the proper conditions) often show a significant tendency to crystallize. The study of morphological behavior of these semi-

flexible polymers becomes especially interesting from a general polymer crystallization viewpoint. Most theories put forward to explain the observed morphologies in flexible polymers (like the L-H theory to explain and interpret the lamellar morphology) cannot be readily applied to these significantly more rigid chain systems. Several fundamental assumptions inherent in such theories will not hold for these materials. Yet for most of these semicrystalline polyimides similar morphological forms such as spherulites, linear growth rates of spherulites, lamellar morphology and SAXS evidence indicating the typical variation of long spacing with undercooling has been demonstrated[21,22,24,27,28]. The following section examines the information on crystallization behavior of this different class of materials and illustrates the various similarities with the flexible chain systems.

For the commercially produced New-TPI, Hsiao[25] et al. have demonstrated the presence of negative spherulites that exhibit thermal nucleation. While the spherulites showed a smooth periphery at lower crystallization temperatures, the morphology at higher temperatures was coarse. The growth rates were found to be linear and could be measured across the growth rate maximum due to lower nucleation density and slower growth rate. Such general spherulitic morphology has also been observed for most other semicrystalline polyimides.

Muellerleile and Wilkes[3] et al. demonstrated the presence of a sheaf like morphology for LaRC-CPI, with higher nucleation density and smaller structures observed on the glass side as compared to "air" side. The growth rates of these structures were found to be linear. To determine the growth rates, SEM was performed on samples quenched after varying amounts of crystallization time[3]. A specific etching cycle was developed to enhance the contrast[15]. Brandom and Wilkes[16,17] observed a spherulitic structure for LaRC-CPI-2 using TEM. Interestingly, the development of the structure was non-uniform with the presence of an amorphous layer often observed for the "air" surface. For LaRC-TPI, Muellerleile[24] et al. observed that any morphological details of the crystalline superstructure could not be enhanced by any microscopic techniques. However, SAXS measurements revealed a long spacing value of ca. 200 Å. For New-TPI, Srinivas et al.[29] and others[11,12,30,31,32] utilized SAXS to demonstrate the presence of long spacing. They also demonstrated the variation of lamellar thickness with

crystallization temperature, a typical behavior for flexible crystalline polymers. Surprisingly, 'regime analysis' has also been carried out for several of these polyimides and regime II→III transition has been reported[.25]. For New-TPI, the regime analysis was performed by Hsiao[25] et al. using the standard values of the constants and $T_m°=406°C$. The product of surface energies $\sigma\sigma_e$ was calculated to be 1176 erg^2/cm^4. It needs to be emphasized that such regime analysis is inherently erroneous for such rigid chain systems as it is based on the applicability of L-H theory to such rigid chain systems, an incorrect assumption. Secondly the equilibrium melting points are not known with any reasonable degree of certainty. Small variations in the value of equilibrium melting point can lead to artificial creation and disappearance of regimes. Thus such an analysis has little fundamental meaning.

Cheng[4] et al. performed a regime analysis for a series of polyimides with varying amounts of ethylene glycol units. They observed that the product $\sigma\sigma_e$ was changed from 760 erg^2/cm^4 to 740 erg^2/cm^4 when the chain flexibility was increased by varying the number of ethylene glycol units from 1 to 3. The authors conjectured that as the lateral surface energy σ would be a constant, the decrease in $\sigma\sigma_e$ with increasing chain flexibility reflects a decreasing value of fold surface energy σ_e for the more flexible polymers. These conclusions although seemingly correct are based on very shaky experimental evidence. Firstly the linear spherulitic growth rates were not utilized but rather a $t_{0.05}$(5% crystallinity) values were used instead. Secondly, and more importantly, the values of the $T_m°$ were approximated to be 10°C above the DSC melting point. Slight changes in the value of $T_m°$ can have a tremendous effect on the value of the product $\sigma\sigma_e$. Therefore putting any meaning to changes of less than 2% in $\sigma\sigma_e$ when using big assumptions to estimate the values of constants is dangerous.
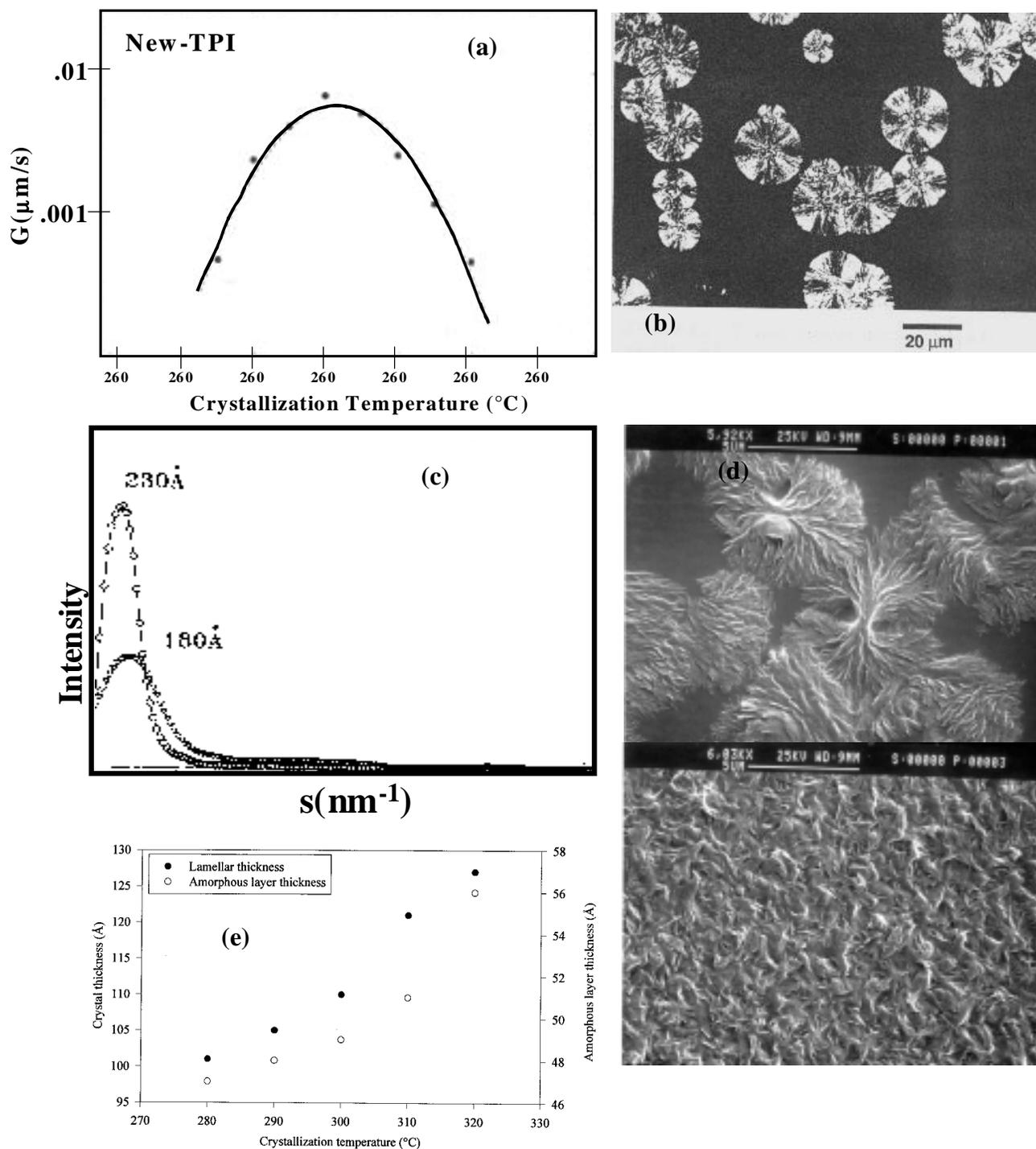
Figure 3.4 (a) Spherulitic growth rates for New-TPI[25]. (b) Negatively birefringent spherulites observed for New-TPI. (c) SAXS for LaRC-CPI-2 samples indicating differently thick lamellae responsible for different endotherms[24]. (d) The hedritic structure obtained for LaRC-CPI by Muellerleile et al[3]. (e) The variation of lamellar thickness for New-TPI observed by Srinivas et al.[22]

3.5 Melting Behavior of Semicrystalline Polyimides

Multiple melting behavior that is a characteristic of a large variety of semicrystalline polymers has also been observed for other more rigid chain materials like PEEK[33,34,35,36] and the polyimides described earlier in this chapter[4,11,17,20]. The presence of multiple melting endotherms can occur due to a variety of reasons like the presence of distinct lamellar populations, different crystal structures and continuous melting and recrystallization process. In this regard, the presence of a small endotherm 10-20°C above the crystallization temperature is a common occurrence and is usually explained on the basis of a secondary crystallization process. Muellerleile et al[3]. observed such behavior for the LaRC-CPI samples. Brandom et al[17]. observed double endotherms for LaRC-CPI-2 at 334°C and 364°C and explained it on the basis of dual lamellar populations. It was theorized that a thickening process was occurring which enabled the thinner lamellae to transform in to thicker ones by a recrystallization process, the kinetics of this being dependent upon the molecular weight of the polyimide. For New-TPI[25], only a main higher melting peak was observed after crystallization at different temperatures. The presence of a small endotherm at T_c+10°C was attributed to the secondary crystallization process although sufficient evidence to prove this has not been presented. Kreuz at al.[28] synthesized a series of BPDA based copolyimides based on 134APB and 1,12-dodecanediamine and observed a triple melting behavior. The polyimide based on BPDA and 134 APB is also the subject of this study. The lowest melting endotherm was again attributed due to the secondary crystallization whereas the middle melting endotherms was explained on the basis of crystallites formed at the previous crystallization temperature[27]. The highest melting endotherm was shown to be the result of melting and recrystallization process with its strength being heating rate dependent. Similar conclusions were later also reached for 134APB-based polyimide by Srinivas et al[20].

Apart from the study by Srinivas et al. it seems that the attribution of different melting peaks (though seemingly correct) has been heavily influenced by evidence from PEEK. Although PEEK itself attracted extensive attention from different research groups

on the cause of multiple melting endotherms the conclusions reached for the various semicrystalline polyimides have been based on relatively smaller amount of experimental evidence. Detailed heating rate studies or Synchrotron SAXS analysis has been lacking in this area.

3.6 Melt Viscosity

Apart from a few handfuls of studies that deal with the rheological behavior of these materials, most research groups have largely ignored this very important aspect. This may be that most such polyimides have been introductory or only in initial stages of development. This is in small part also due to relatively high melting temperatures usually required by these materials and the lack of widespread availability of appropriate equipment for such experimental work. Some available examples of this work would be illustrated here.

Figure 3.5 depicts the shear loss modulus, shear storage modulus and the calculated complex viscosities for two grades of LaRC-TPI 1500 series polyimide[18]. The time sweep experiments (Figure 3.5) at 350°C show the behavior up to 3 hours and illustrate good stability at this relatively low melt temperature of 350°C. While the medium flow grade sample (MFG) remained unchanged, the high flow grade (HFG) sample showed an increase from 8000 to 45,000 dynes/cm^2 during the time frame of the experiment. Figure 3.5 illustrates the frequency sweep experiments at different melt temperatures and the calculated complex viscosity values are plotted. Apart from lower temperatures, a significant change in the viscosity-frequency profile or a clear shear-thinning behavior was not observed. These values were, however, utilized to construct a master plot (Figure 3.5) which enabled the predictions at a broader range of frequencies. The reference temperature was fixed at 320°C and the shift factors obtained did not show any dependence on the molecular weight. The authors thus concluded that the molecular weights were above the critical molecular weight for entanglement, M_c. It is also clear that the MFG grade was a higher molecular weight polymer. Additionally, the authors utilized the data to make predictions about the molecular weight distributions of the two samples. The ratio of the molecular weights was found to be ca. 1.6 and the molecular weight distribution was proposed to be approximately equal.
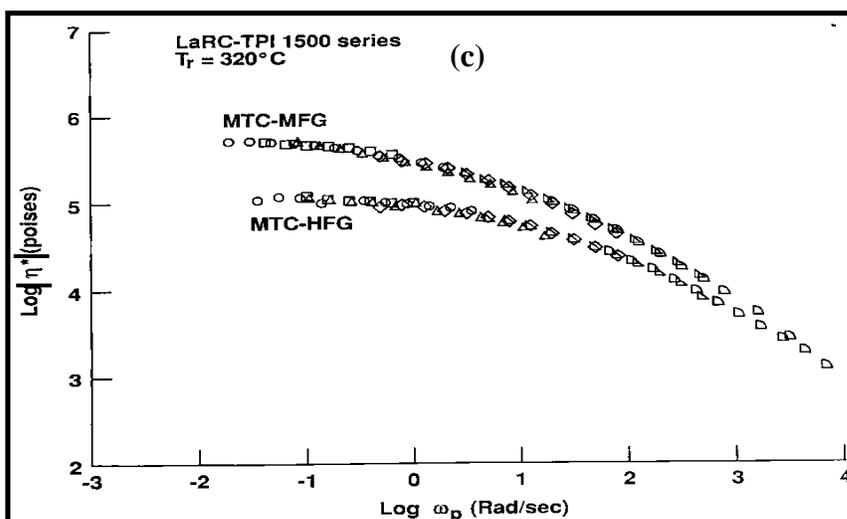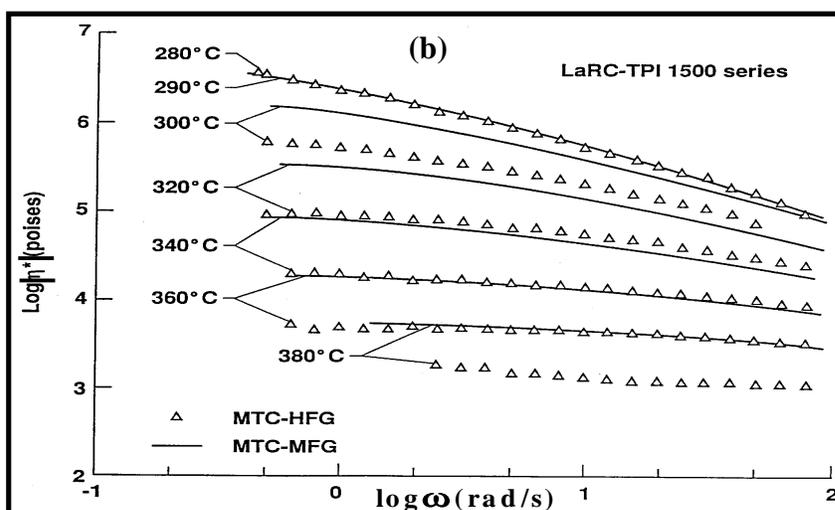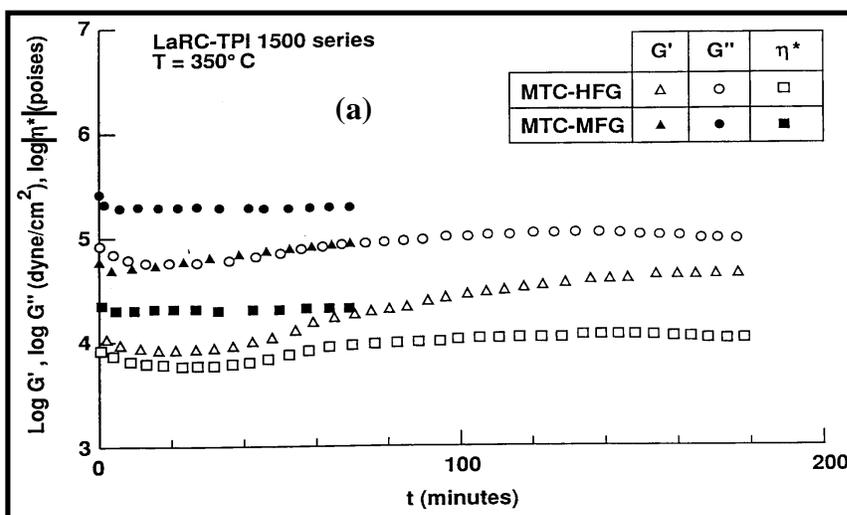
Figure 3.5 Rheological results for different grades of LaRC-TPI.[18] (a) Loss modulus, storage modulus and complex viscosity at 350°C for up to 3 hrs. (b) Complex viscosity-frequency profiles at different melt temperatures for two grades of LaRC-TPI. (c) Master curves for the two grades constructed using the data in (b).

Figure 3.6 shows the viscosity frequencies profiles by Hergenrother et al.[37] for a polyimide adhesive. Also shown are two comparative scans of Ultem PEI and a polysulfone adhesive. It is, however, not clear as to what the authors were comparing because not only are the polymers of different molecular weights, but the scans are also run at different temperatures. Also, it is clear that for the polyimide, the complex viscosity values at 10 Hz (a common comparative frequency) are very high at ca. 10^6 poise (or 10^5Pa.s). It is important to mention that regardless of the annealing treatments at various temperatures this polyimide did not crystallize after having been taken once above the melt temperature. Hence the polyimide serves no utility from the crystallization viewpoint.

Figure 3.6 however, shows viscosity results for a more promising polyimide, LaRC-8515[38], a polyimide which also has given excellent adhesion results[39]. The polyimide chains are endcapped with phthalic anhydride and the dianhydride used is BPDA. The number 8515 in the name refers to the % of two different diamines used, 3,4'-ODA (85%) and 1,3-bis (3-APB) (15%). Consecutive time sweeps are illustrated at different melt temperatures, each being for a duration of 30 minutes. The polyimide displays significant thermal stability at all temperatures. The plot also illustrates the temperature dependence of the storage and loss moduli and depicts the crossover to a more solid-like behavior at 340°C (indicated by G">G'). The recrystallization ability of this interesting system is also indicated in Figure 3.6. Although the polyimide is not readily crystallizable, 1 hour annealing at 325°C is successful in reintroducing the crystallinity. Detailed DSC work to characterize the crystallization behavior has not been
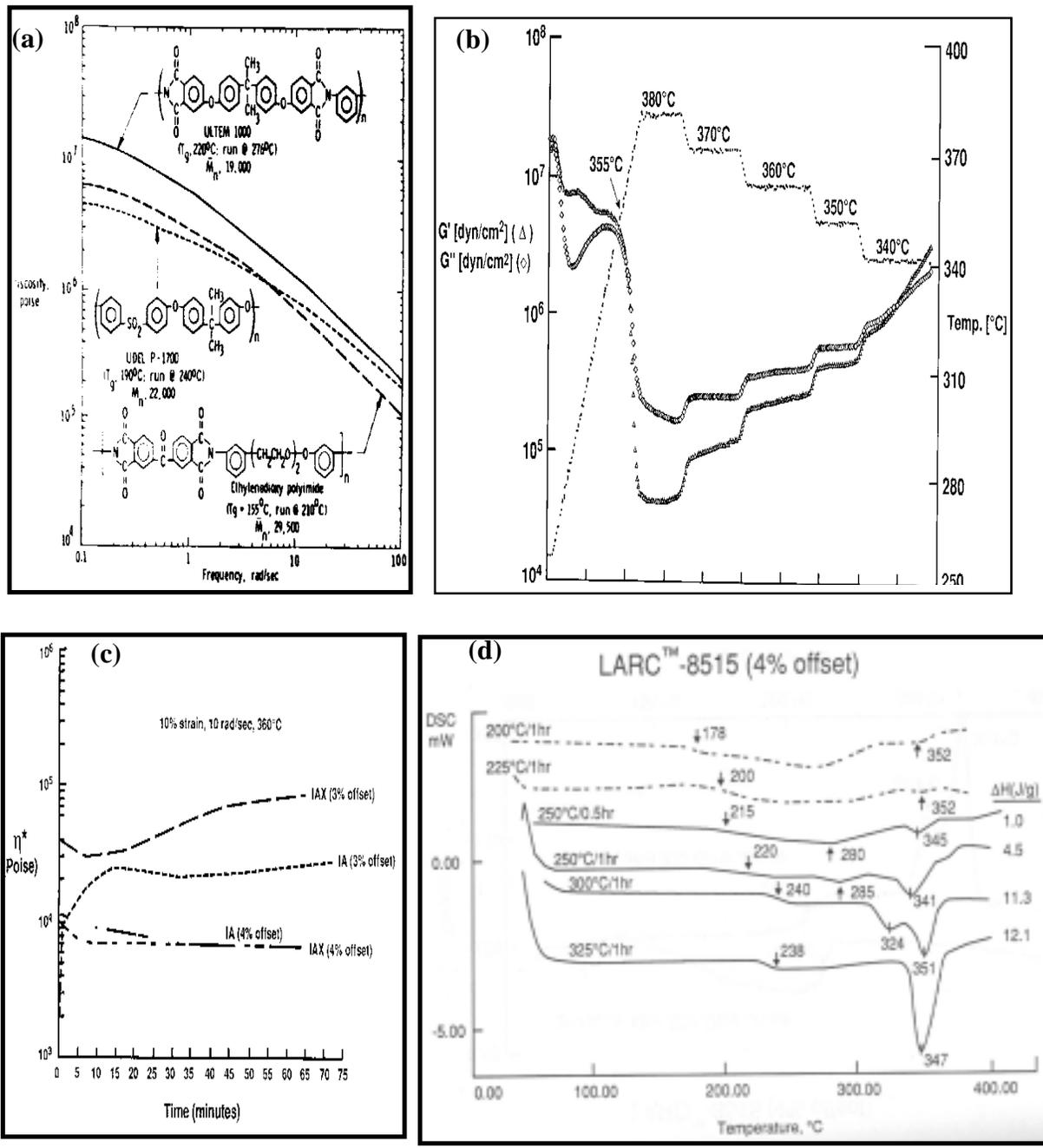
Figure 3.6 (a) Melt rheology of an amorphous polyimide by Hergenrother et al.[37] (b) Continuous loss and storage shear modulus for LaRC-8515 polyimide at different melt temperatures[38] (c) Melt viscosity vs. time at 360°C for LaRC-IA and –IAX[40] (d) Crystallization behavior of LaRC-8515 after annealing at different temperatures.

conducted on this polyimide so far. However, it is safe to say that the kinetics of crystallization of the polyimide would be poor due to narrow window of crystallization.

The results for two other NASA thermoplastic polyimides, LaRC-IA and LaRC-IAX are shown[40] in Figure 3.6. Significant thermal stability at a relatively low melt temperature of 360°C is shown for the polyimides. The chemical structure of the polyimides is based on ODPA dianhydrides with the chains endcapped with phthalic anydride. The diamine utilized for LaRC-IA is 3,4'-ODA while for LaRC-IAX a mixture of 3,4'-ODA (90%) and p-PDA (10%) is used. The chemical structures of the monomers are shown below.
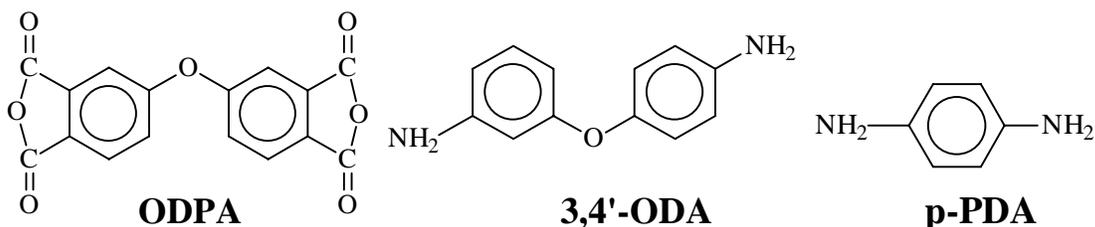
Scheme 3.1   Monomers used in LaRC-IAX synthesis[40].

Detailed crystallization work on this polyimide is however not available. Figure 3.7 shows the rheological behavior for New-TPI at different melt temperatures[9]. DSC results on the crystallization behavior of this polyimide have already been discussed earlier in this chapter. Thermal stability at such high melt temperatures is relatively poor with higher temperatures leading to a faster increase in viscosity. Substantial chain extension/crosslinking seem to be occurring at these temperatures leading to the viscosity increase[9]. It is useful to recall the earlier discussed results, which indicate that this polyimide loses its recrystallization ability catastrophically once exposed to these melt temperatures for even a short duration of time[20]. Results are also presented in Figure 3.7 for the polyimide TPEQ-ODPA characterized in this laboratory[19,22]. Although the chains were endcapped with phthalic anhydride the stability of the polyimide is poor with large increases in viscosity occurring in the melt. This is in large part due to the very high melting point associated with this polyimide thus requiring still higher melt temperatures.
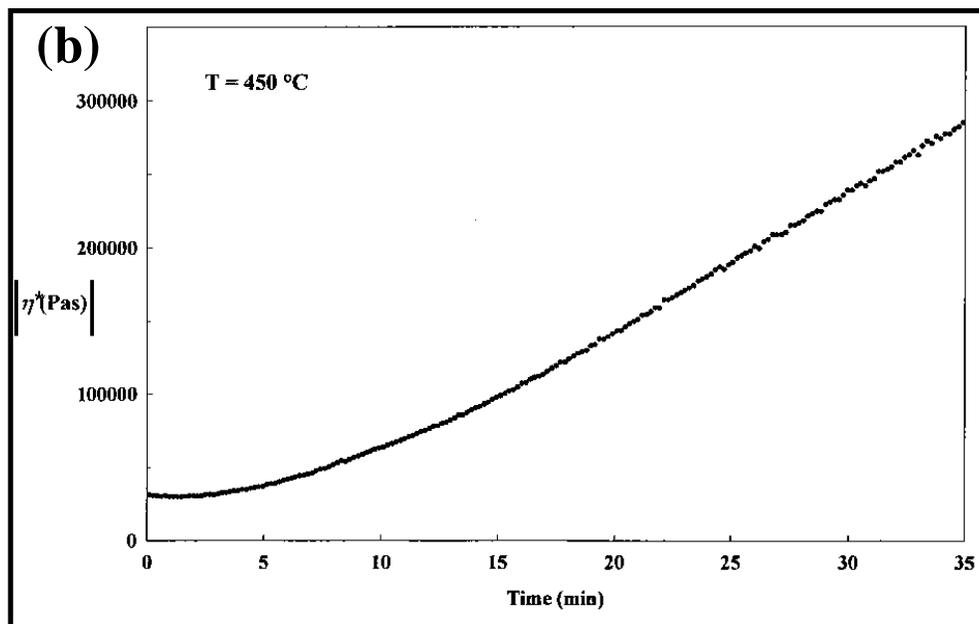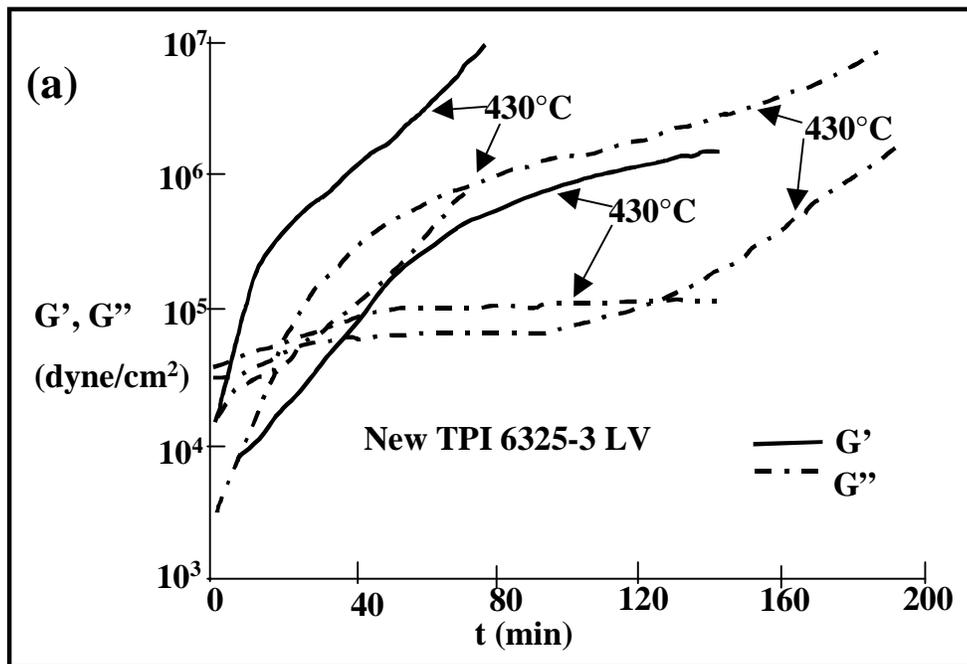
Figure 3.7   Rheological behavior of (a) New-TPI[9] and (b) TPEQ-ODPA polyimides showing molecular weight changes for both polyimides[19].

References:

[1] St, Clair, T.L. in *Polyimides* Eds. Wilson, D., Stenzenberger, H.D. and Hergenrother, P.M., 1990, Chapman and Hall, New York, pg. 58.

[2] Hergenrother, P.M. and Havens, S.J. in *Polyimides: Materials, Chemistry and Characterization* Eds. Ferger *et. al*. Elsevier, New York, 1989.

[3] Muellerleile, J.T., Risch, B.G., Rodrigues, D.E., Jones, D.M. and Wilkes, G.L. *Polymer* 1992, **34**, 789.

[4] Heberer, D.P., Cheng, S.Z.D., Barley, J.S., Lien, S.H., Bryant, R.G. and Harris, F.W. *Macromolecules* 1991, **24**, 1890.

[5] Tamai, S., Yamaguchi, A. and Ohta, M. *Polymer*, 1996, **37**, 3683.

[6] Tamai, S., Oikawa, H., Ohta, M. and Yamaguchi, A. *Polymer*, 1998, **39**, 1945.

[7] Product Literature, "*New-TPI*" Mitsui Toatsu Chemicals, Inc.

[8] Yamaguchi, A. and Ohta, M. Proceed. 18th Int. SAMPE Tech. Conf., Oct 1986, pg. 229.

[9] Hou, T.H and Redy, R.M. *SAMPE quarterly*, Jan 1991, **22** (2), 38.

[10] Hirade, T., hama, Y., Sasuga, T. and Seguchi, T. *Polymer*, 1991, **32** (14), 2499.

[11] Huo, P.P. and Cebe, P. *Polymer* 1993, **34** (4), 696.

[12] Friler, J.B. and Cebe, P. *Polym. Eng. Sci*. 1993, **33** (10), 587.

[13] Okuyama, K., Sakaitani, H. and Arikawa, H. *Macromolecules* 1992, **25**, 7261.

[14] Muellerleile, J.T., York, G.A. and Wilkes, G.L. *Polym. Commun*. 1991, **32**, 176.

[15] Muellerleile, J.T. and Wilkes, G.L. *Polym. Prepr*. 1990, **31**, 637.

[16] Brandom, D.K. and Wilkes, G.L. *Polymer* 1994, **35**, 5672.

[17] Brandom, D.K. and Wilkes, G.L. *Polymer* 1995, **36**, 4083.

[18] Hou. T.H. and Bai, J.M. *High Performance Polymers* 1990, vol. **2**.

[19] Srinivas, S., Graham, M., Brink, M.H., Gardner, S., Davis, R.M., McGrath, J.E. and Wilkes, G.L. *Polym. Eng. Sci*. 1996, **36**, 1928.

[20] Srinivas, S, Caputo, F.E., Graham, M., Gardner, S., Davis, R.M., McGrath, J.E. and Wilkes, G.L. *Macromolecules* 1997, **30**, 1012.

[21] Brandom, D.K. *Ph.D. Thesis*, Virginia tech. June 1996.

[22] Srinivas, S. *Ph.D. Thesis*, Virginia Tech. June 1996.

[23] Product Literature, "High Performance Polyimide- LaRC-TPI" Mitsui Toatsu Chemicals, Inc.

[24] Muellerleile, D.K. *Ph.D. Thesis*, Virginia Tech. September 1991.

[25] Hsiao, B.S., Sauer, B.B. and Biswas, A. *J. Polym. Sci. Part B* 1994, **32**, 737.

[26] Cebe, P. and Hong, S.D. *Polymer* 1986, **27**, 1183.

[27] Hsiao, B.S., Kreuz, J.A. and Cheng, S.Z.D. *Macromolecules* 1996, **29**, 135.

[28] Kreuz, J.A., Hsiao, B.S., Renner, C.A. and Goff, D.L. *Macromolecules* 1995, **28**, 6926.

[29] Srinivas, S. and Wilkes, G.L. Polymer .

[30] Huo, P.P., Friler, J.B. and Cebe, P. *Polymer* 1993, **34**, 4387.

[31] Brillhart, M.V. and Cebe, P. *J. Polym. Sci. Part* B 1995, **33**, 927.

[32] Lu, S.X., Cebe, P. and Capel, M. *J. Appl. Polym. Sci*. 1995, **57**, 1359.

[33] Bassett, D.C., Olley, R.H. and Raheil, I.A.M.A. *Polymer* 1988, **29**, 1745.

[34] Blundell, D.J. and Osborn, B.N. *Polymer* 1983, **24**, 953.

[35] Blundell, D.J. Polymer 1987, 2248.

[36] Cheng, S.Z.D. Cao, M.Y., Wunderlich, B. *Macromolecules*, 1986, **19**, 1868.

[37] Harris, F.W., Beltz, M.W. and Hergenrother, P.M. *SAMPE Journal*, **Jan/Feb** 1987, 6.

[38] Hou, T.H., Wilkinson, S.P. and Jensen, B.J. *Polyimides: Trends in Materials and Applications, Proceedings of the Fifth International Conference on Polyimides*, 1994, 409.

[39] Hou, T.H., Wilkinson, S.P. and Jensen, B.J. *40th International SAMPE Symposium* **May**, 1995, 1072.

[40] Chang, A.C., Hou, T.H. and St. Clair, T.L. *Trends in Materials and Applications, Proceedings of the Fifth International Conference on Polyimides*, 1994, 3.