

# Investigation of Crystalline Changes in LaRC-TPI Powders

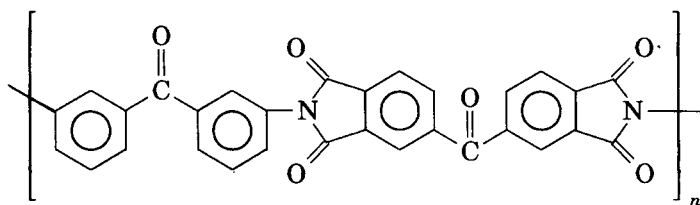
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## Synopsis

Semicrystalline LaRC-TPI is known to be capable of recrystallizing to higher melting crystalline forms upon initial melting. The behavior of these different crystalline forms has not been studied before. The present study uses techniques of differential scanning calorimetry and X-ray diffractometry to investigate these crystalline structural changes during recrystallization of this material. Semicrystalline LaRC-TPIs synthesized from three different laboratories are included in this work.

## INTRODUCTION

The NASA Langley Research Center-Thermoplastic Polyimide (LaRC-TPI) is a linear aromatic polyimide developed in the late 1970s. This material has been used as a high temperature adhesive and composite matrix resin.<sup>1-3</sup> Recently two companies, namely Mitsui Toatsu Chemical Co. or MTC America and Rogers Corp., have attained licensing agreements with NASA to further develop and commercialize this polymer. A crystal melt endotherm was first noted in a commercial LaRC-TPI powder from Mitsui Toatsu during calorimetric analysis. Such semicrystalline structure had not been evident in other versions of LaRC-TPIs that had been previously examined. Subsequently a semicrystalline LaRC-TPI was also synthesized at Langley Research Center by means of a chemical cyclodehydration scheme.<sup>4</sup> The thermal and rheological properties of both semicrystalline LaRC-TPIs have been studied.<sup>4-8</sup> Somewhat later Rogers supplied a semicrystalline LaRC-TPI to NASA. It was found that these LaRC-TPIs were capable of recrystallizing to higher crystal melting temperature forms upon initial melting at approximately 275°C. The present study was undertaken to study the crystalline structural changes during this recrystallization of the three different versions of semicrystalline LaRC-TPIs:



LaRC-TPI

## EXPERIMENTAL

### Materials

Three different crystalline LaRC-TPI powders were investigated. Two of these were supplied by the Mitsui Toatsu Co. of Japan (Lot 72-501), designated hereinafter as MI, and Rogers Corp. in Connecticut (Lot 10), designated hereinafter as RO. These powders were used as received without further treatment. A third LaRC-TPI crystalline powder studied (designated as LA) was developed in-house at the Langley Research Center. The scheme used for cyclodehydration during the synthesis of this material has been reported elsewhere.<sup>4</sup>

### Sample Preparation

A two-piece steel mold was preheated inside an oven to the desired annealing temperature. Four annealing temperatures of 250, 280, 300, and 320°C were chosen for this study. The oven atmosphere was circulating dry nitrogen gas, and the mold had provision for a cavity that measured  $3 \times 7 \times 0.5$  in. A 1.2 g sample of each of the above-mentioned powders was then placed inside the cavity and was subsequently annealed for 22 h. Samples prepared in this way (i.e., inside preheated steel blocks) exhibited excellent reproducibility as measured by DSC. The annealed specimens were then reground into powder form for further characterization studies.

### Differential Scanning Calorimetry (DSC)

Specimens of 3.0 mg size were encapsulated in aluminum pans and heated in a DuPont 1090 DSC at a rate of 20°C/min over the range 40–400°C. The glass transitions and melting endotherms were monitored and recorded. Sample weight of 3.0 mg was always held constant to eliminate variability associated with sample size so that the areas under the recorded melt-endotherm peaks could be compared directly.

### 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° ( $2\theta$ ) was recorded on hard disk for the angular range 5–40° ( $2\theta$ ). An external  $\alpha$ -quartz standard was used in goniometer alignment.

## RESULTS AND DISCUSSION

The polymerization and crystallization behavior of MI and LA LaRC-TPI powders subjected to various thermal treatments has been studied and reported<sup>4–8</sup> earlier. The initial melting of these powders shows a peak temperature at around 275°C. For the MI material, it was found<sup>5–7</sup> that, at annealing

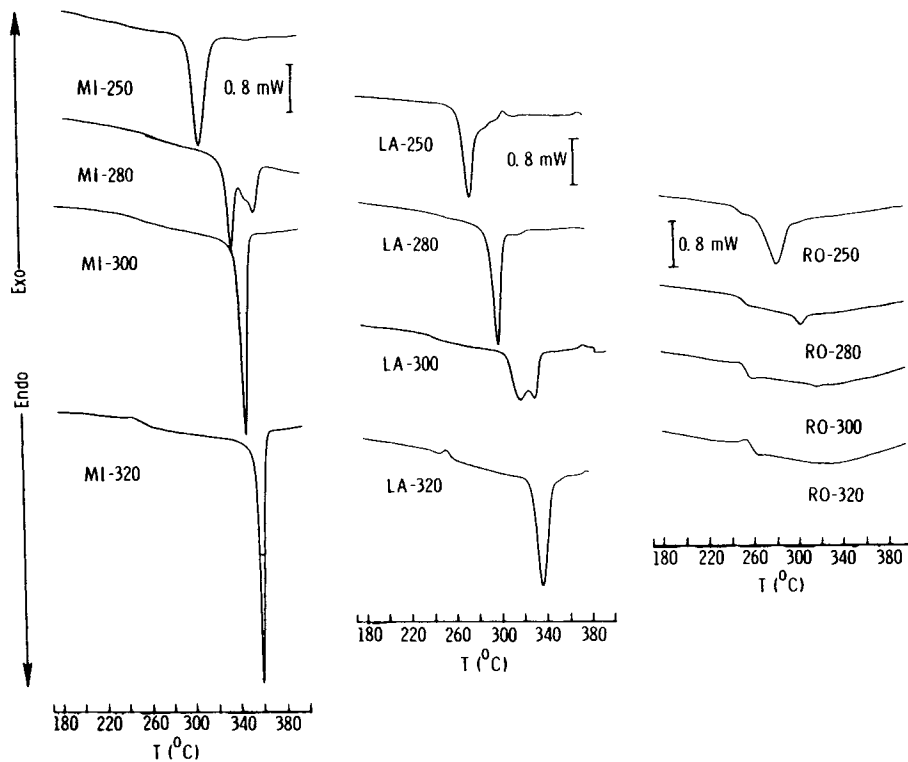


Fig. 1. DSC thermograms of the three different semicrystalline LaRC-TPIs annealed for 22 h at the temperatures indicated.

temperatures below 320°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. The LA material was found<sup>1</sup> to behave similarly, except that the critical annealing temperature is 340°C instead of 320°C. Four annealing temperatures, 250, 280, 300, and 320°C were, therefore, selected for the present study. An annealing time of 22 h was adopted to insure a fully developed crystallinity in each sample.

The DSC thermograms of these annealed LaRC-TPI powders are shown in Figure 1. The glass transition temperature  $T_g$  can be estimated from the inflection point on the thermogram; the melting temperature  $T_m$  was taken from the endothermic peak. These transition temperatures are tabulated in Table I. Also included in the table are the heat of fusion calculated from the area under the endothermic melting peak in each of the thermograms, which represents the crystallinity in the sample. These areas can be compared directly since the sample weights used in the thermal analyses were held constant, and the scales plotted on both the vertical and horizontal axes for each thermogram are identical. At each isothermal annealing condition, the MI LaRC-TPI material consistently exhibited the highest crystallinity (fusion endotherm area), while the RO material exhibited the lowest.

The fresh MI LaRC-TPI has been proposed to have lower initial molecular weight than the LA material because of low inherent viscosity and an initial

TABLE I  
Transition Temperatures and Heats of Fusion for the Annealed LaRC-TPI Powders

Sample <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	$T_{m1}$ (°C) <sup>c</sup>	$T_{m2}$ (°C) <sup>c</sup>	$T_{m3}$ (°C) <sup>c</sup>	$\Delta H$ (J/g) <sup>d</sup>
MI-250	218	278	323	—	31.6
MI-280	238	306	319	326	32.2
MI-300	252	348	—	—	31.6
MI-320	260	368	—	—	29.3
LA-250	—	278	—	—	22.1
LA-280	248	302	—	—	22.3
LA-300	248	321	334	—	23.0
LA-320	257	338	—	—	26.0
RO-250	250	283	—	—	15.5
RO-280	252	305	—	—	2.11
RO-300	255	319	—	—	0.5
RO-320	260	—	—	—	0.0

<sup>a</sup> First two letters denote source of material. MI = Mitsui Toatsu Co., LA = NASA Langley Research Center, RO = Rogers Corp. The number that follows represents annealing temperature in °C. Annealing time is 22 h in all cases.

<sup>b</sup> Glass transition temperature estimated at the inflection point.

<sup>c</sup> Peak melting temperatures in increasing order for multiple peaks situation.

<sup>d</sup> Heat of fusion calculated from the area under endothermic peak.

low glass transition as evidenced by DSC thermal analysis.<sup>4</sup> Mitsui has proposed that the low viscosity and glass transition may be due to isoimide and amide acid units in the polymer backbone.

The intermolecular oligomer nucleation type was considered as a likely nucleation path for MI LaRC-TPI during the crystallization reaction.<sup>6,7</sup> A certain oligomer concentration must first be formed by a homogeneous reaction step before nucleation can occur and the crystallization during polymerization can commence.<sup>9</sup> The higher crystallinity possessed by the MI LaRC-TPI sample, as compared to the others, was therefore attributed to its lower initial molecular weight, which enhances the formation of the necessary level of oligomer concentration during the initial polymerization stage. Based on such a hypothesis, the RO LaRC-TPI should have the highest initial molecular weight among the three materials studied here. This has in fact been confirmed indirectly by the rheometer measurements of the melt flow properties, which indicate that RO LaRC-TPI generates the least flow upon melting.<sup>10</sup>

The glass transition temperatures  $T_g$  vs. annealing temperatures for the three LaRC-TPIs are plotted in Figure 2. The 320°C annealing for all three materials approaches the nominal  $T_g = 260^\circ\text{C}$  attainable for the LaRC-TPI. The MI LaRC-TPI shows the biggest change in  $T_g$  with respect to the annealing temperature. The large difference in  $T_g$  among the samples annealed at 250°C (which is below the initial melting temperatures of all samples) is also consistent with the observations of crystal formations during isothermal annealing as discussed above.

The thermograms shown in Figure 1 offer limited information about the possible differences in crystalline structures among samples. For example, while the various crystalline LaRC-TPI powders have been produced by

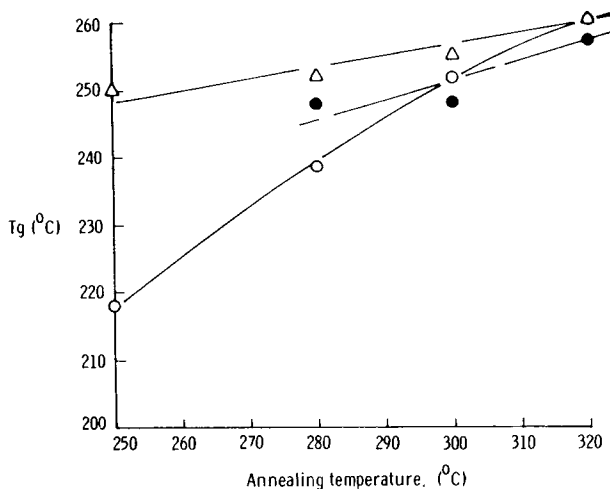


Fig. 2. The glass transition temperatures vs. annealing temperatures for the three LaRC-TPIs. ( $\Delta$ ) RO; ( $\bullet$ ) LA; ( $\circ$ ) MI. Annealing time is 22 h in all cases.

chemical cyclodehydration,<sup>4</sup> the differential scanning calorimetry suggests that the MI LaRC-TPI material may have been subjected to thermal post-treatment after the cyclodehydration. However, nothing about the structural differences among samples annealed at 250°C can be drawn from the thermograms in the figure alone, except that a recrystallization occurs in LA samples after the initial melt. In addition, for a given material, both single and multiple melting peaks are observed in the thermograms for samples annealed at different elevated temperatures. This may indicate that, after the initial melt, the crystalline phases formed during the recrystallization could be different and dependent upon the annealing temperatures. X-ray scattering measurements were conducted to resolve these questions.

The X-ray diffractograms for the samples listed in Table I are shown in Figure 3. All of the endothermic crystalline melting peaks shown in the thermograms in Figure 1 are confirmed by the existence of crystalline reflections at various  $2\theta$  angles on the diffractograms, except for samples RO-280, RO-300, and RO-320, where the crystallites in the samples are either nonexistent or are too small to be resolved in the diffraction patterns, adding their broad diffraction contribution to the amorphous halo.

Comparisons among the diffractograms of MI-250, LA-250, and RO-250 reveal noticeable structural differences in the fresh LaRC-TPI powders prepared by different means mentioned earlier. The diffractograms of LA-250 and RO-250 are essentially identical. Both show three major reflections in the  $2\theta = 14\text{--}28^\circ$  range and two minor ones located at the extremes of the diffractogram. The diffractogram of LA-250 is similar to that of RO-250 but displays higher peak to background intensities. On the other hand, the MI-250 LaRC-TPI shows four major reflections at the center and two minor ones at the extremes. While a direct comparison of the degree of crystallization is not valid for the initial MI and LA specimens since they possess different crystalline structures, the LA and RO materials are comparable, and

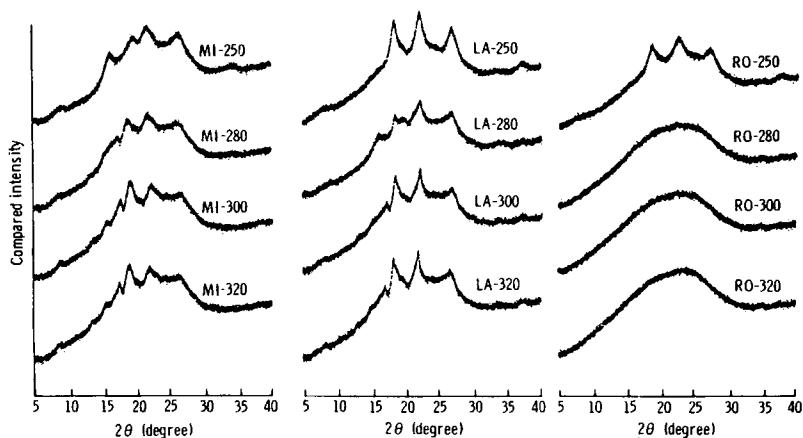


Fig. 3. X-ray diffractograms of the three crystalline LaRC-TPIs annealed for 22 h at the temperatures indicated.

their comparison in Figure 3 suggests a higher degree of crystallization for the LA material. This finding is confirmative of the analysis derived from the thermal studies with its implication of lower initial molecular weight for the LA material as compared to the RO material and is consistent with the differences in flow properties mentioned above.

At elevated temperatures, the samples melt and recrystallize to form new crystalline phases. The two diffractograms MI-300 and MI-320 are considered essentially identical, that of MI-280 being transitional between MI-250 and MI-300. Although the peak temperatures at melt were noted from the thermograms of Figure 1 to increase consistently with the increasing annealing temperatures, and in the MI-280 case, multiple melting peaks were formed, when compared with the fresh MI-250 sample in Figure 3, the reflections are seen to rearrange to new  $2\theta$  values with one of the minor reflections at the high  $2\theta$  end diminished.

The three X-ray diffraction patterns of LA-280, LA-300, and LA-320 at elevated annealing temperatures can also be found in Figure 3. The diffractograms of LA-300 and LA-320 closely resemble those of MI-280, MI-300, and MI-320 discussed above, despite the fact that they are produced by the annealing samples with different crystalline structures (i.e., the initial crystalline structure of LA-250 vs. MI-250), and that they exhibit noticeable differences in thermograms, with different peak melting temperatures as well (see Fig. 1).

The diffractograms of MI-250 and LA-280 are plotted in Figure 4 for comparison. Also included in this figure is the diffractogram of a sample (designated as LA-280C) taken from the coarser particles precipitated from the synthesis. This sample was also annealed at 280°C for 22 h. All the LA LaRC-TPI diffractograms shown in Figure 3 are for samples taken from the much finer powders precipitated in the same batch of synthetic material as opposed to the LA-280C. It can be noted that the diffractogram of LA-280C closely resembles that of MI-250, which is the initial crystalline phase exhibited in the MI LaRC-TPI powders.

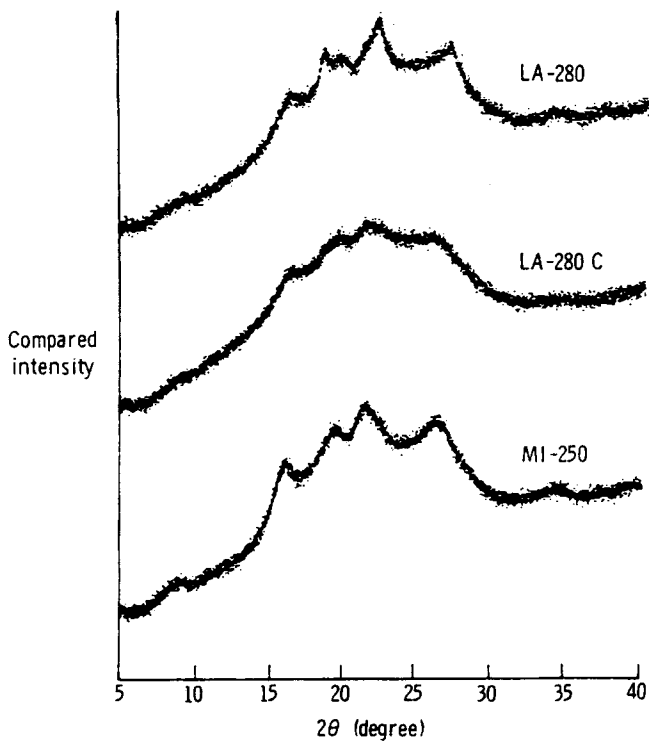


Fig. 4. Comparisons of X-ray diffractograms of three semicrystalline LaRC-TPIs.

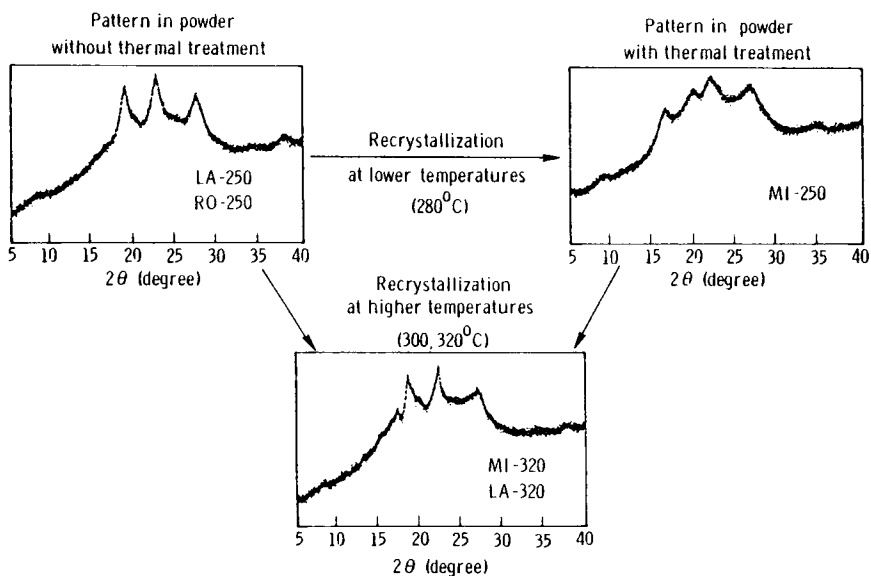


Fig. 5. Transformation of crystalline phases of the LaRC-TPIs.

A scheme of transformations of crystalline structures for the LaRC-TPI materials investigated here can, therefore, be constructed as shown in Figure 5. The starting crystalline LaRC-TPI powders synthesized by chemical cyclodehydration with and without thermal treatment possess distinctively different crystalline phases as illustrated by the X-ray diffractograms of LA-250 and RO-250 vs. MI-250. Recrystallizations of the LA LaRC-TPI at low temperature (e.g., 280°C) after initial melting transforms the crystalline phase to one similar to that of the MI-250 sample. Recrystallizations of the crystalline LaRC-TPIs at higher temperatures (e.g., 320°C) after melting, however, will produce a new structural form illustrated by the diffractograms of MI-320 and LA-320.

### CONCLUSIONS

Three versions of crystalline LaRC-TPI powders have been evaluated. These materials were synthesized by different techniques in different laboratories by chemical cyclodehydration. Each material possessed an initial melt endotherm in the 275–285°C temperature range. These materials were capable of recrystallizing to higher melting temperature forms after the initial melts. Investigations by means of DSC and X-ray scattering techniques were used to characterize the crystalline structural phase transformations after recrystallization. These techniques were found to be complementary in the study of these structural changes.

Crystallinity as measured by the area under the melt-endotherm peak in the DSC thermogram shows strong dependence on initial inherent viscosity. The high levels of crystallinity noted in the Mitsui LaRC-TPI recrystallized samples are possibly attributable to the low MWs that exist in the as-received powders or the presence of chain flexibilizing groups such as isoimides or amides. This low MW or chain flexibility may enhance the capability of forming a sufficient level of nucleation sites for crystallization.

Distinctively different X-ray diffractograms are noted between fresh LaRC-TPIs synthesized by Mitsui and those from NASA or Rogers. It was found that the recrystallization of all synthesized LaRC-TPI samples at lower temperatures (e.g., 280°C) resulted in X-ray diffraction patterns identical to that of Mitsui LaRC-TPI, which may have been subjected to a thermal treatment during processing. A third crystalline structural phase was found to exist in all of the LaRC-TPIs when they were recrystallized at higher temperatures (e.g. 300, 320°C).

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