Solvent-induced crystallization of aromatic polyimide

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(Received 26 July 1988; accepted 29 September 1988)

N-methyl-2-pyrrolidinone (*N*MP) solvent was found to induce crystallization of chemically imidized polyimide (LARC-TPI) from the amorphous state at elevated temperatures. Multiple melting endotherms of TPI were revealed by differential scanning calorimetry (d.s.c.) thermograms after treatment with *N*MP. Both the quantity of solvent and the treating time affect the crystallinity.

(Keywords: LARC-TPI polyimide; *N*MP solvent; solvent induced crystallization; d.s.c. thermograms; crystalline phases)

INTRODUCTION

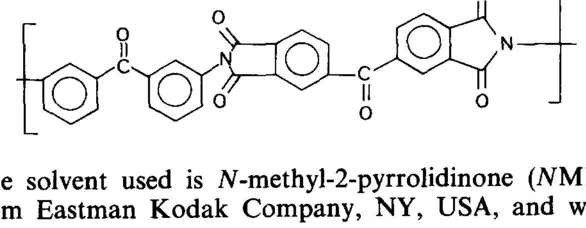
The thermoplastic polyimide, LARC-TPI, is useful as a high performance resin for aerospace and electronics applications. This material, originally developed by NASA Langley Research Center[1–5], was thermally imidized and completely amorphous. Later, the Mitsui Toatsu Company prepared a chemically imidized powdered material in which a crystalline transition at about 272°C was observed[6,7]. The crystalline transition temperature increased with time upon annealing between the melting point and 330°C. A completely amorphous material resulted at annealing temperatures above 330°C. A similar material in powder form, also prepared by chemical imidization, exhibited a non-reversible melting transition at about 288°C. No annealing-enhanced crystallization has been observed.

Because of the presence of residual solvents in as-received LARC-TPI powders[6–8], it was suspected that solvent in the TPI might play a role in its crystallization. Thus, the effect of solvent, specifically *N*-methyl-2-pyrrolidinone (*N*MP), on the crystallization of TPI powders was investigated. Our initial findings are the topic of this paper.

EXPERIMENTAL

Material

The LARC-TPI powders were prepared and provided by Rogers Corporation, CT, USA. The structure is:



The solvent used is *N*-methyl-2-pyrrolidinone (*N*MP) from Eastman Kodak Company, NY, USA, and was distilled before use.

Thermal analysis

Thermal properties of LARC-TPI were determined using a Perkin–Elmer differential scanning calorimeter (DSC-2) at a scan rate of 5° min^{-1}. The samples weighed from 10 to 15 mg, and were tested under dry nitrogen.

Treatment procedure

Before exposing the TPI powders to *N*MP, their previous crystallinity was erased by heating the powders to 310°C in argon-filled sealed tubes for 20 min. The erasure was verified by a d.s.c. scan. Two groups of TPI powder samples (0.1 g per sample in Group 1 and 0.3 g per sample in Group 2) were placed in glass tubes with narrow necks, having 2.4 ml volume below the necking point. *N*MP solvent was then added, the tubes were sealed at the neck under vacuum, and kept at 200–205°C for one hour. In a third group of samples (Group 3), TPI powder was added to glass capillary tubes, 9 cm long and 1.6 mm in diameter. Then *N*MP, in a proportion of about 2:1 by volume to TPI powder, was added, and the tubes were sealed under 1 atm†. The treatment took place in a salt bath with tubes standing in vertical positions at 160 ± 10°C for various times. After contact, the products were removed from the tubes, ground, washed with THF, and then dried in a vacuum oven at 120°C for 3 d.

In another experiment, treated product from Group 2 was heated to 360–365°C for 15 min and then exposed once again to *N*MP. The experiment was similar to that described for Groups 1 and 2 above.

RESULTS AND DISCUSSION

Solvent treatment

A small amount of TPI powder could be dissolved after prolonged exposure to the *N*MP. No apparent crystallization was observed directly from the solution. A certain degree of sintering of the TPI powder occurred during the treatment, with the sintered TPI appearing permeable to the solvent molecules.

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† 1 atm ≈ 10^5 Pa

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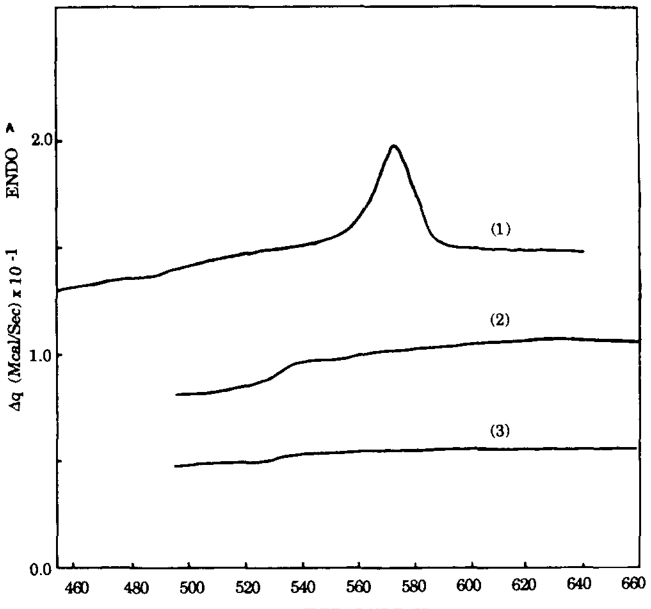

Figure 1 D.s.c. thermograms of TPI before exposure to *N*MP: (1) as received TPI; (2) second heating scan; (3) after erasure of crystallinity

The treatment temperature for Groups 1 and 2 was close to the boiling point of *N*MP, which is 202°C at 1 atm. Hence, the pressure within the glass reaction chamber was roughly 1 atm, although the overall pressure in Group 1 was probably slightly higher due to the lower vacuum upon sealing at ambient temperature. The pressure within the tubes in Group 3 was also close to 1 atm, because the glass tubes were sealed at 1 atm and the treatment temperature of 160°C was far below boiling point of *N*MP.

Thermal properties

The as-received TPI powder displayed a melting endotherm at 288°C, with $\Delta H_m = 10.7\,\mathrm{cal\,g^{-1}}$†, as shown on the d.s.c. thermogram in *Figure 1* (Curve 1). After cooling, a second heat scan was carried out to determine if any residual crystallinity remained. The second heating scan is shown as Curve 2 of *Figure 1* and indicates that the material is amorphous, with a glass transition of 258°C. Curve 3, comparable to Curve 2, presents a d.s.c. scan of the sample after thermal treatment and before the addition of *N*MP. Thus, at the point of introduction of solvent, the crystallinity of the TPI powder has been completely erased.

The d.s.c. thermograms of the samples in Group 1 in the first heating scan after treatment with *N*MP are shown in *Figure 2*. There are two clearly separate melting peaks, one at around 300°C and the other at around 350°C. The curves are arranged in order of increasing size of the high melting endotherm. The sum of the two melting enthalpies is close to $6.2\,\mathrm{cal\,g^{-1}}$ for the first four of five samples, as shown in *Table 1*. If the difference in molar enthalpy of the two crystalline phases is neglected, the total crystallinity of heat treated samples is estimated to be 63% of the crystallinity of the as-received TPI powder. Only one high melting peak is observed in the last sample, which has about 70% of the crystallinity of as-received TPI. As is the case with the as-received TPI, no evidence of crystallinity is observed after cooling and reheating of these samples. (Interestingly, the bimodal melting of these samples resembles the behaviour of TPI powders, supplied by Mitsui Toatsu Company, after annealing at 280°C for different times[6].) The only difference among the five samples in Group 1 is the quantity of the solvent placed in the treatment chamber. This suggests that the *N*MP content in TPI affects the nature of the crystalline phases.

Figure 3 presents the d.s.c. thermograms of the samples in Group 2, in which the *N*MP to TPI weight ratio is varied from 0.155 to 1.61. A clear trend exists in that the ratio of the enthalpy of the high melting peak to that of the low one increases as the solvent content increases. However, the total crystallinity is lower at higher solvent content. It should be mentioned that at the lowest solvent content, there was insufficient liquid to wet all of the TPI powder surface, while at the highest *N*MP content all of the TPI powders were visibly wet and some were partially immersed under *N*MP liquid. There appears to be a range of melting peaks at temperatures between 300

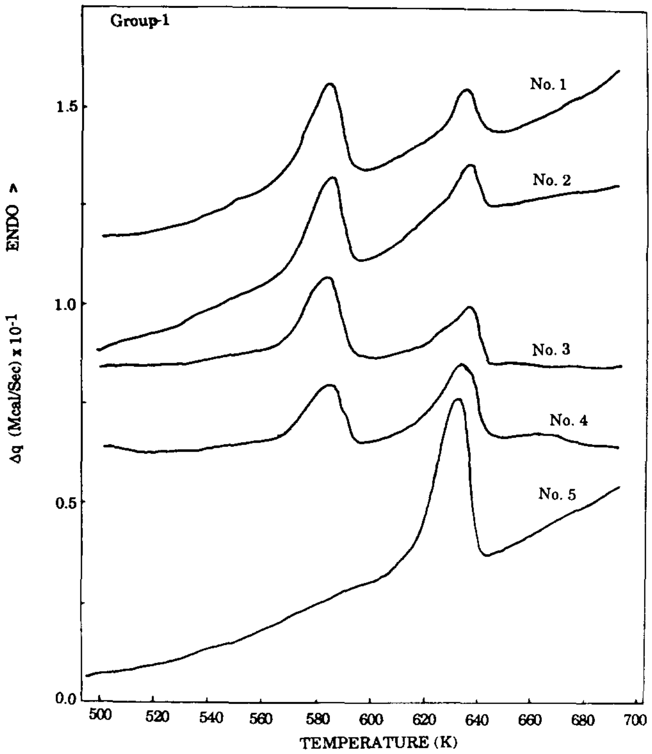

Figure 2 D.s.c. thermograms of TPI after exposure to *N*MP at 200°C for 1 h (Group 1). Numbers on curves correspond to the sample numbers in *Table 1*

Table 1 Enthalpies of fusion for *N*MP-treated LARC-TPI samples in Group 1

Sample no.	$\Delta H^a_{m,1}$ (cal g^{-1})	$\Delta H^b_{m,2}$ (cal g^{-1})	$\Delta H_{m,1}+\Delta H_{m,2}$ (cal g^{-1})
1	4.44	1.87	6.31
2	3.75	2.53	6.28
3	3.46	2.79	6.25
4	2.60	3.73	6.33
5		7.37	7.37

[a] $\Delta H_{m,1}$ is melt enthalpy at ≈300°C
[b] $\Delta H_{m,2}$ is melt enthalpy at ≈350°C

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† 1 cal≈4.2 J

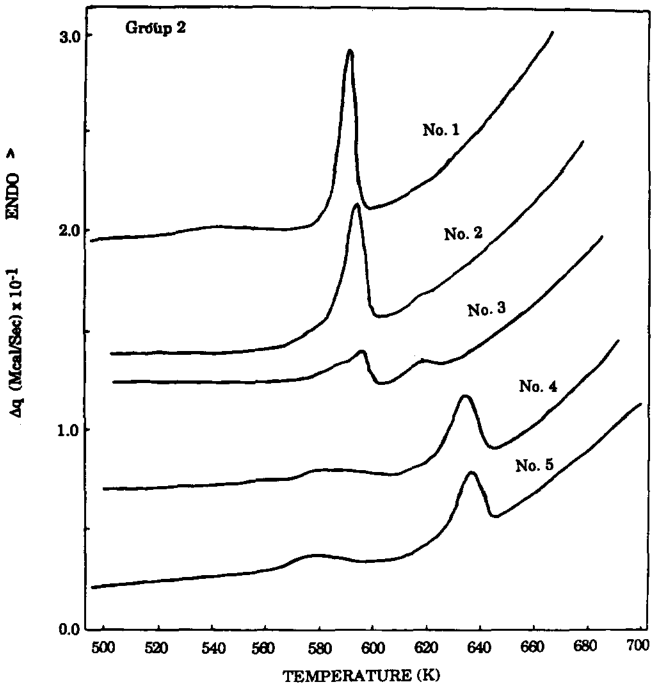

Figure 3 D.s.c. thermograms of TPI after exposure to *N*MP as a function of *N*MP/TPI weight ratio: 1, 0.15; 2, 0.54; 3, 0.93; 4, 1.45; 5, 1.61 (Group 2)

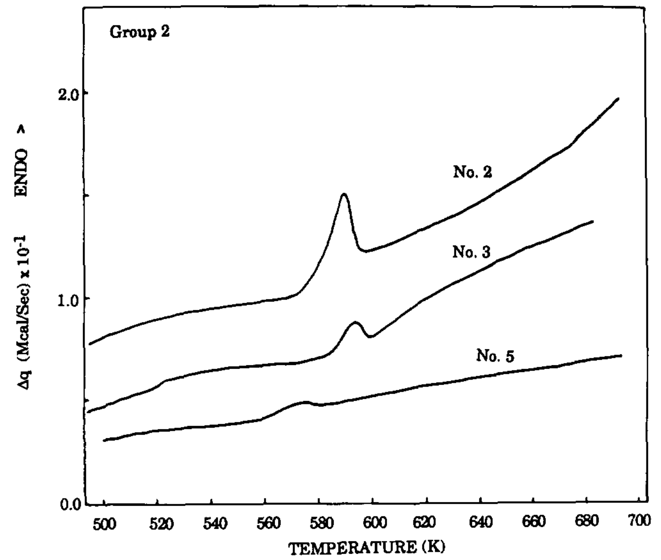

Figure 4 D.s.c. thermograms of TPI after a second exposure to *N*MP as a function of *N*MP/TPI weight ratio: 2, 0.54; 3 0.93, 5, 1.61 (Group 2)

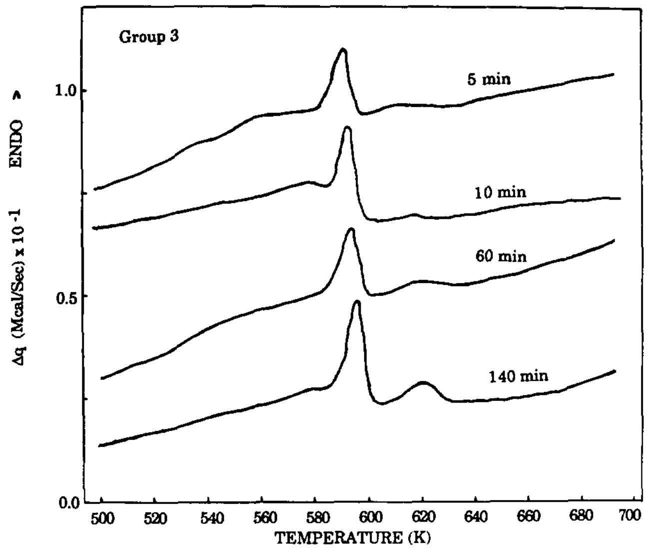

Figure 5 D.s.c. thermograms of TPI after exposure to *N*MP at 160±10°C as a function of time (Group 3)

and 350°C. One might interpret these results by assuming either the existence of multiple crystalline lattices of TPI or compatible mixtures of at least two crystalline phases. Another interpretation might be that the shift of melting temperatures reflects the level of lattice defects in a specific crystal structure.

The samples of Group 2 were reheated to 360°C for 15 min to erase all traces of crystallinity. Most of the samples were severely decomposed due to exposure to high temperature, but three among five samples still showed return of crystallinity after the treatment with *N*MP, as shown in *Figure 4*. This result confirms a role of solvent molecules in the recrystallization of TPI.

The TPI powders in Group 3 were completely immersed in liquid *N*MP and the treatment temperature was well below the boiling point of *N*MP. The results of d.s.c. scans are shown in *Figure 5*. As can be seen, the crystallinity of both phases increases with time. The high melting phase appeared later but grew faster with the increase of treatment time.

The results illustrate that either high *N*MP content or extended interaction time favour the formation of a higher melting crystalline phase, and that the crystallization process is dependent upon whether the contact is with vapour or liquid. There are a number of possibilities. One is that a non-uniform concentration of *N*MP within the TPI matrix causes the formation of different crystalline phases. Another is that the lower melting crystalline phases are gradually transformed to the higher melting phase during the treatment. Higher solvent content may stimulate a faster crystallization rate, accompanied by a rapid crystalline phase transformation. The last effect is attributed to the changes in both molecular weight and molecular weight distribution upon thermal treatment, which undoubtedly affect the crystallization behaviour[9].

In general, neither the extent of solvent/powder contact nor the pressure were well defined during the treatment. One could imagine that the crystallization behaviour might depend strongly on whether the TPI powders were only wet on the surface or were completely saturated with *N*MP liquid, and that the thermodynamics as well as the rate of crystallization might depend on the treatment pressure. It is not clear whether thermally imidized materials will behave similarly.

CONCLUSIONS

Although the mechanism of crystallization is not yet understood, the preliminary results indicate that *N*MP solvent can induce the crystallization of chemically imidized LARC-TPI. The crystalline phases are related to the solvent content and treatment time. These findings open up many possibilities for improving processing conditions and final properties of the material.

ACKNOWLEDGEMENT

Financial support from DARPA/ONR contract no. N0014-86-K-0772 and Connecticut Cooperative High Technology Research and Development Grant Program are gratefully acknowledged.

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