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Uniaxial Stretching of Poly(keto-ether-imide) Films

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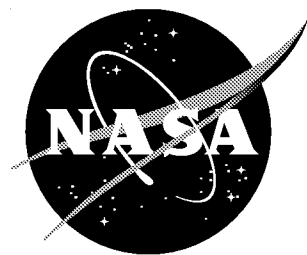
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Abstract

Fully-cured aromatic polyimides were prepared from various combinations of five dianhydrides and six diamines. When heated progressively under constant load, most of the films elongated rapidly near their glass transition temperatures. In about half of the nineteen materials, the strain was self-limiting – a possible indication of strain-induced crystallinity. The presence of crystallinity was established unambiguously for one material.

Introduction

Polyimide films are durable, radiation-resistant materials that are useful as electrical insulation, in thermal blankets, as windows and barrier films, as supports in structures such as deployable solar arrays, and potentially, in solar sails and large inflatable platforms or reflectors. It is of interest to try to orient polyimides because the stiffness, strength and dimensional stability of most glassy or crystallizable polymers can be improved by stretch-orientation. In fact, commercial films such as Kapton® (DuPont) and Upilex™ (Ube) are probably biaxially oriented.

Stretching is also commonly used to improve piezoelectric and photorefractive materials. As polyimides are considered for these applications, it will be useful to understand how they respond to stretching.
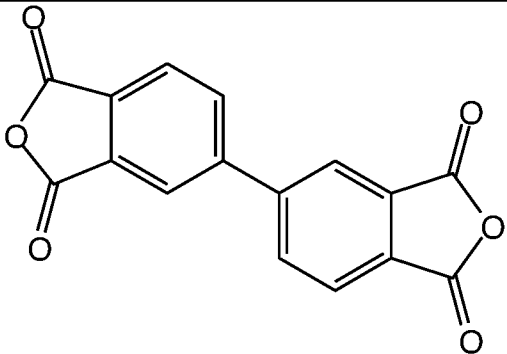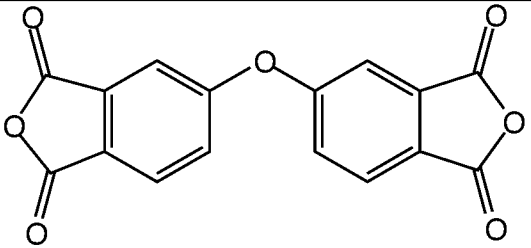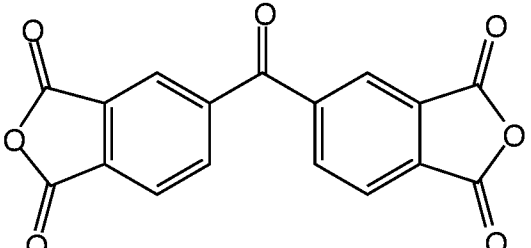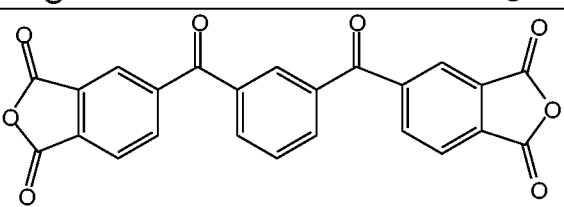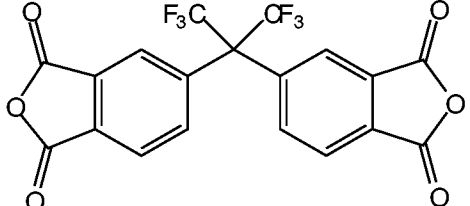
The two-step synthesis of polyimides[1] provides two opportunities to introduce orientation. First, the soluble amic acid precursor may be stretched. It may be possible to maintain or enhance the orientation as the succeeding imidization reaction is carried out thermally or chemically. This approach has been used both with fibers[2] and with films.[3] A disadvantage is the difficulty of managing a stretching process that is coupled with simultaneous solvent outgassing and a high-temperature curing reaction.
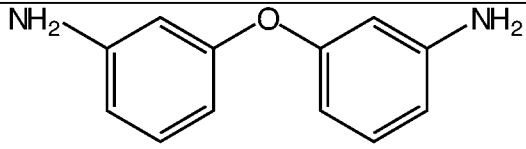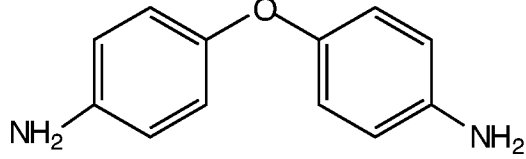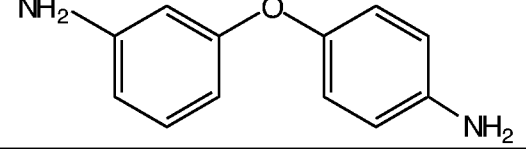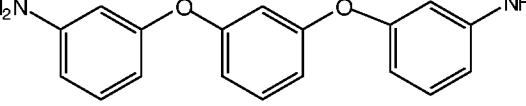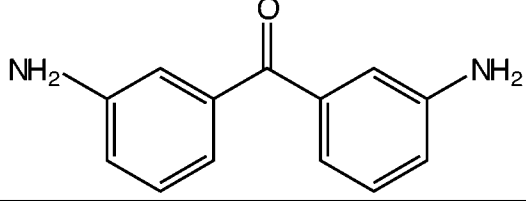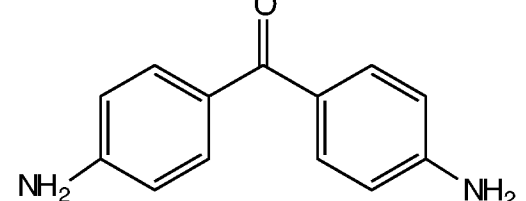
A second and potentially simpler alternative is to stretch the fully-imidized material.[4] This requires that the polymer in question behave as a thermoplastic; fortunately, many such materials have been discovered. In the present feasibility study, 19 different fully-cured polyimides were screened using thermal deformation analysis (TDA). The TDA technique, which involves heating to progressively higher temperatures under a constant load, has been useful in the qualitative study of stretch-induced crystallization.[5]

Experimental

Each polyimide was prepared from stoichiometric amounts of purified diamine and dianhydride.[6] Acronyms are summarized in Table 1.

Table 1. Polyimide Monomers

Dianhydrides	Structure
BPDA	
ODPA	
BTDA	
IDPA	
6FDA	

Diamines	
3,3'-ODA	
4,4'-ODA	
3,4'-ODA	
1,3-APB	
3,3'-DABP	
4,4'-DABP	

Films were cast on soda-lime glass plates, dried in a reduced-humidity enclosure at room temperature, and cured in air-circulating ovens at 100°, 200° and 300°C successively, holding for 1 hour at each temperature.

A density gradient column was prepared from aqueous sodium bromide with 2-propanol as a wetting agent.

The thermal deformation apparatus[7] is shown schematically in Figure 1. The film sample was gripped by stainless-steel clamps that were tightened using screws. To prevent slipping and to help prevent film tearing at the grip, a piece of compliant quartz felt was placed between the film and the clamping strip. The initial specimen dimensions between clamps were 13 wide x 20 mm long.

Dead-weight loading was applied via a chain attached to a swivel and a wire that ran over two pulleys to a long-stroke DC displacement transducer. Nominal stress in all cases was 7.0±1.8 MPa.

After the weight was applied, the displacement readout was zeroed at room temperature and the oven temperature was ramped to 350°C. The initial ramp rate was 10°C/min., but above 200°C the oven could only maintain about 4.5°C/min. Noticeable stretching began 18 to 58 minutes into the TDA experiment, depending on the polymer. With this experimental approach, both the strain rate and the ultimate strain are determined by the material behavior rather than being controlled by the apparatus.

Results and Discussion

The TDA traces are assembled in Figs. 2-6. Three distinct regions are evident in the sigmoidal curves. The first region is below the softening point, where very little strain occured. Then, most samples elongated fairly rapidly over a range of approximately 20°C beginning near the glass transition temperature. If the sample did not break at this point, there followed a range of temperatures over which the strain rate was very small again. This plateau at longer times, when it was seen in other polymers, has been attributed[8,9] to strain-induced crystallization.

Although property improvements can be obtained by stretching materials that do not crystallize,[10] crystallization can be helpful. The nascent crystals can serve as physical crosslinks, preventing stress relaxation during the stretching process and allowing a greater degree of orientation to be produced. In addition, crystallizing films can be annealed under stress ("heat set") to stabilize them against relaxation and shrinkage near the glass transition temperature. This raises their use temperatures relative to amorphous materials.

Many thermoplastic polyimides form metastable crystals during solution imidization[11] but with the exception of very rigid or rod-like chains[3,12], they do not usually crystallize spontaneously upon cooling from the melt.[13] It is remarkable, therefore, that of the 19 materials in the present screening study, several became cloudy and 10 exhibited well-defined plateaux in the TDA experiment. Strain-induced crystallization could thus be a very general route to improved properties in aromatic polyimides.

The theory of simultaneous stretching and crystallization is not well developed; most treatments rely heavily on simplifying assumptions.[14] There is even disagreement on whether the enhanced rate of crystallization arises primarily from nucleation or crystal growth.[15,16] It is clear, however, that the degree of orientation created in the amorphous polymer is a key variable.

With this in mind, it appears that among the polymers studied here, those that contain the 3,3'- diamines may have melt viscosities too low to allow efficient orientation. They tend to stretch rapidly and break under constant load. At the other extreme was the 4,4'-DABP/BPDA, which did not stretch appreciably at all even though the starting film is clear and flexible, with a Tg of 302°C. In between, we find for example the polymers containing 3,4'-ODA. These readily strain-harden, which makes them rather forgiving in terms of processing. Although the details of the TDA responses of the individual

polymers may depend somewhat on molecular weight, all the samples in the present study were prepared at the highest molecular weight practical, so it is believed that qualitative comparisons between materials should be valid.

In the discussion above, cloudiness and the leveling-off strain in the TDA experiment were taken as evidence for crystallization. Neither, of course, is definitive. Cloudiness would ordinarily imply the presence of crystallites or voids that are large enough to scatter visible light. In the present experiments stretching also produced a surface roughening, perhaps by accentuating the texture on the surface of the as-cast film. One side of the film remained shiny, however, and was quite featureless in the scanning electron microscope at 1000X. It is not known whether the air side or the side that had been cast against the glass plate became roughened, but the scattering was sufficient to thwart attempts to measure birefringence with prism-coupled or Abbe refractometers. Some of the films appeared to have a sheen that might be produced by light interacting with crazes.

Figure 7 is a differential scanning calorimetry scan of one of the materials that may have crystallized, 3,4'-ODA/ODPA. This particular specimen was stretched isothermally at 260°C. There is a melting peak near 320°C, with a total melting endotherm of 21 J/g. Although the heat of fusion of this polymer is not known, comparison can be made with LARC™-CPI and with Mitsui's Aurum, which have heats of fusion of 92 J/g and 139 J/g of crystals respectively.[17,18] By this estimate, then, the crystallinity of the stretched 3,4'-ODA/ODPA may be as high as 20%. The shape of the DSC curve suggests, however, that there may have been some "cold crystallization" between the Tg (ca. 230°C) and the onset of melting. If a stretched sample is annealed for 30 min at 260°C, it exhibits two endotherms, one at 320°C and a much smaller one with a peak at 275°C. The total heat of melting for the two populations of crystals is ~22 J/g of polymer.

Density is often another useful indicator of crystallinity. Accordingly, stretched and unstretched 3,4'-ODA/ODPA films were compared. Although the oriented film had a tensile modulus in the stretch direction over twice as high as that of an unstretched film, its density (1.3950 g/cm^3) was only 1.1% higher. Given that the crystal density could be expected to be 13% higher than that of the completely amorphous polymer[19], and assuming that there are no unwetted voids, 8% crystallinity would be inferred for this specimen.

Finally, it is known[4] that when 3,4'-ODA/ODPA is stretched isothermally just above Tg, it undergoes strain-induced crystallization when the strain exceeds approximately 2.5. The X-ray diffraction pattern[20] in Figure 8 shows conclusively that 3,4'-ODA/ODPA films stretched isothermally to a strain of 5 are crystalline, with a fiber repeat distance of 20.8Å. A systematic search[21] for extended conformations of this polymer readily finds several with a repeat unit end-to-end length of 20.2Å and an angular mismatch of only 4°; minor adjustments to bond angles and torsions would easily bring this prediction into agreement with experiment.

It seems likely that other polymers among those studied will crystallize well under suitable stretching conditions. TDA provides very useful guidance as a starting point for further (e.g. isothermal) stretching experiments.

6

Conclusions

TDA is a useful screening tool for stretch-orientation. With it, 10 candidates for further optimization were identified. Structural requirements for successful crystallization appear to include both a relatively compact molecular conformation and a high enough melt viscosity just above Tg to sustain a fairly high degree of orientation.

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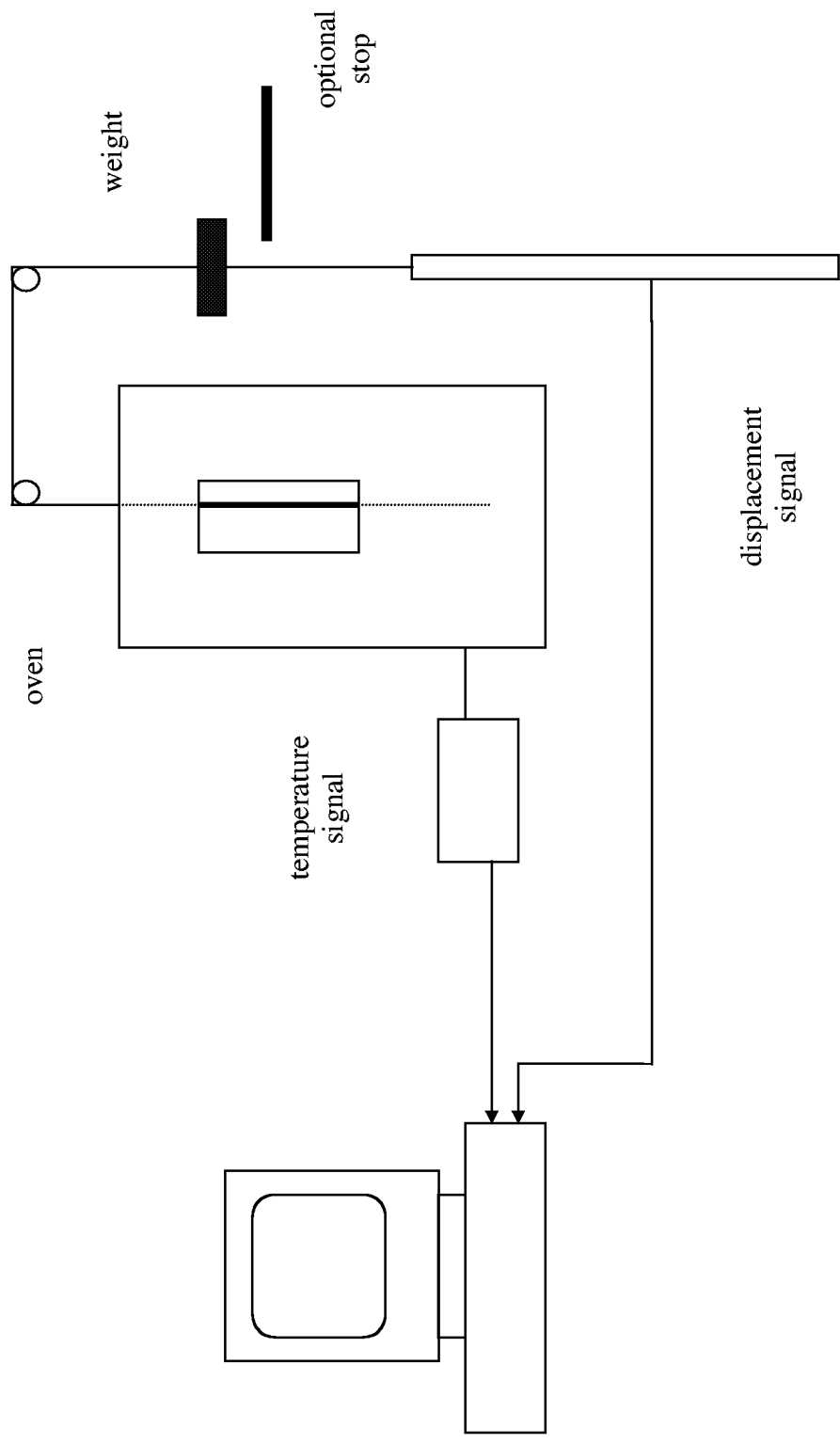signal

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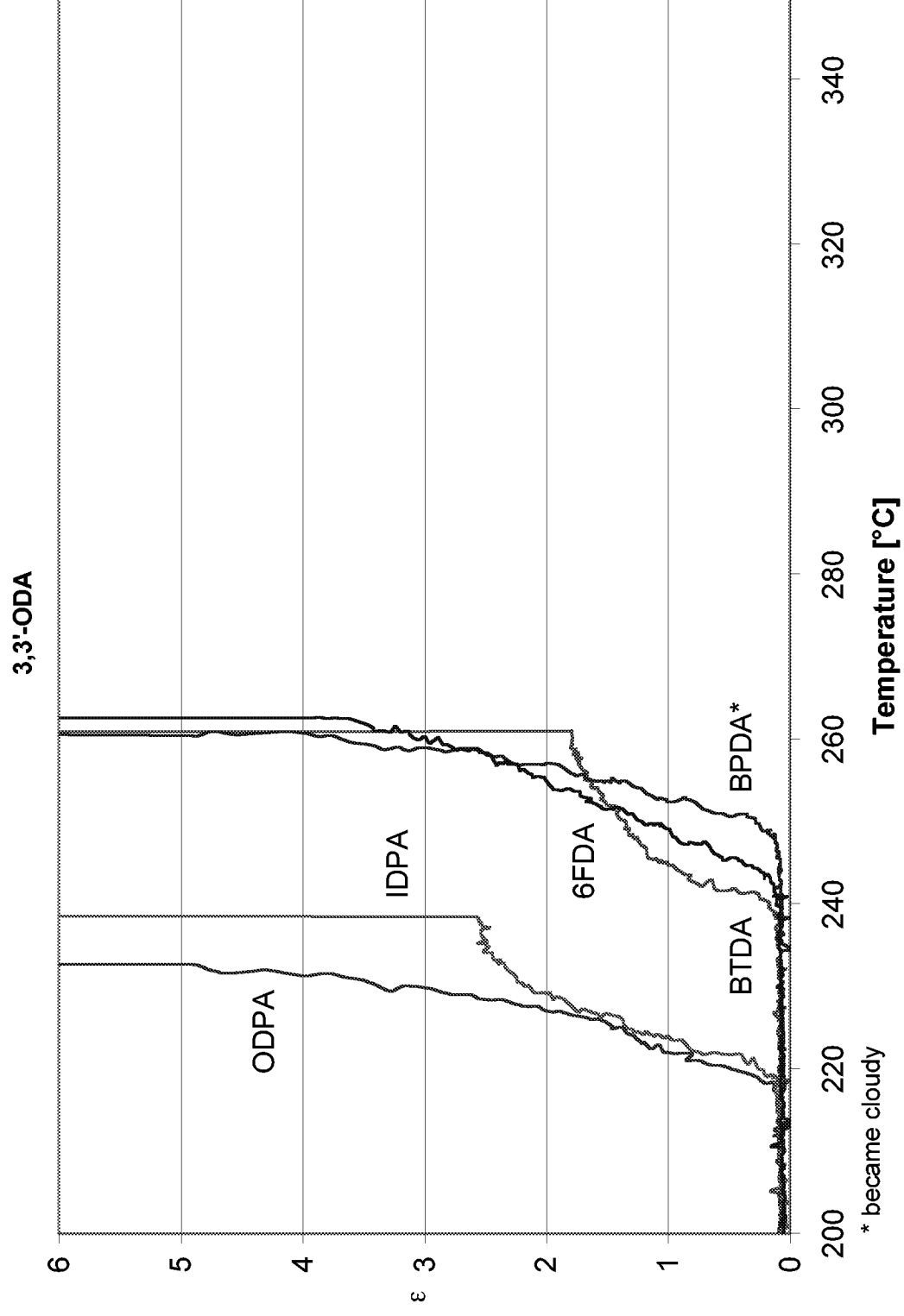
Figure 1. Schematic of TDA apparatus

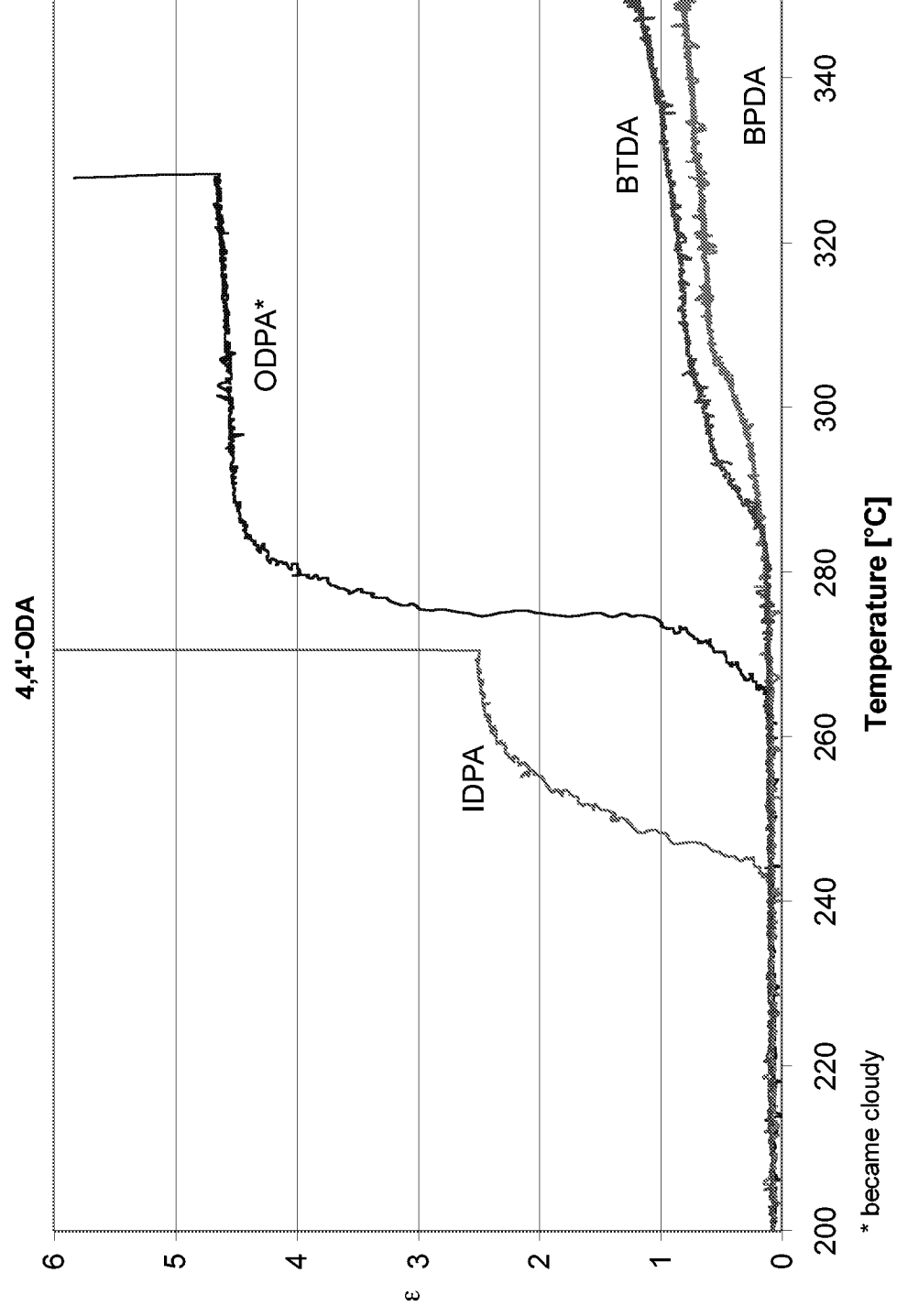Figure 2. TDA behavior of 3,3'-ODA-containing polyimides

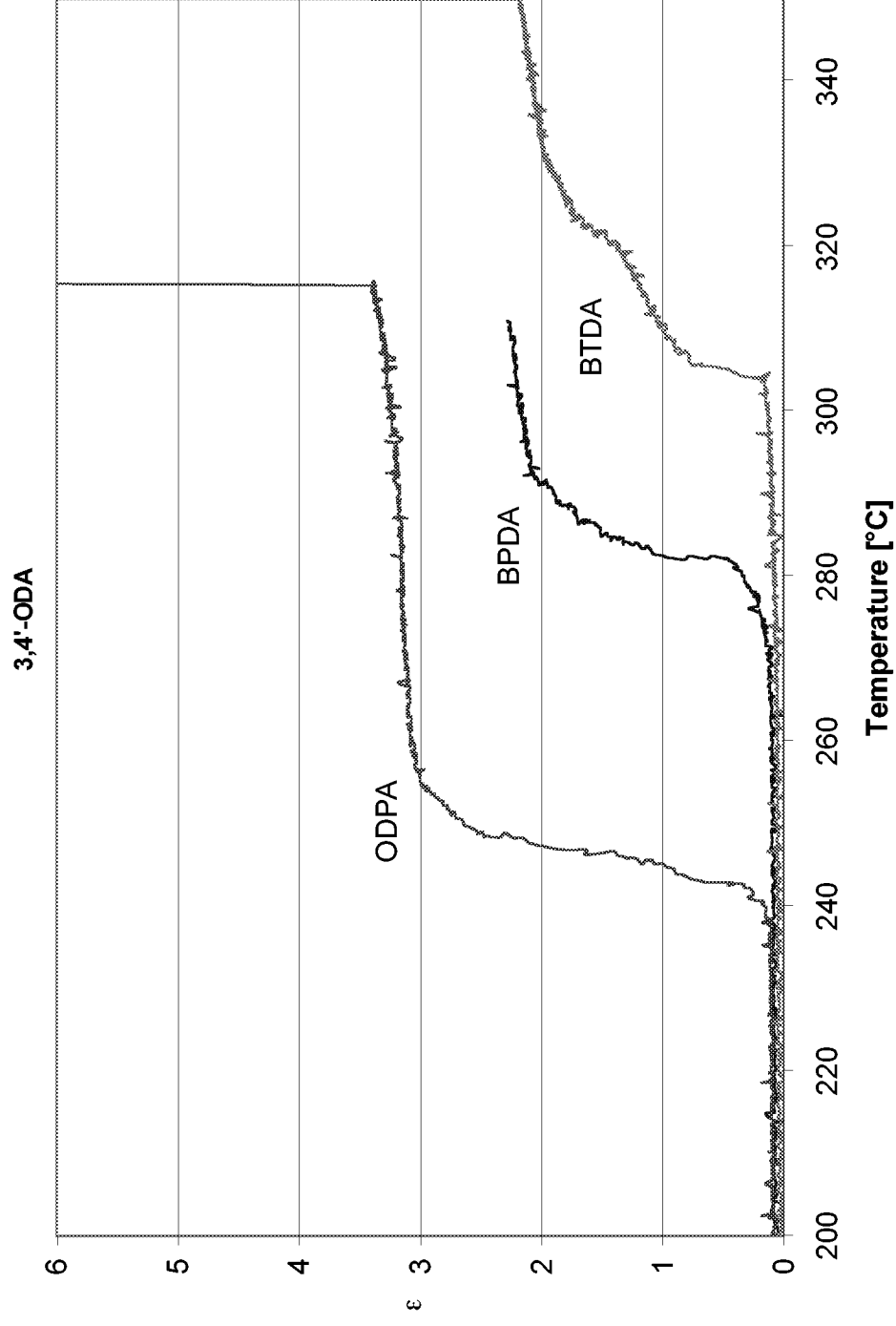Figure 3. TDA behavior of 4,4'-ODA-containing polyimides.

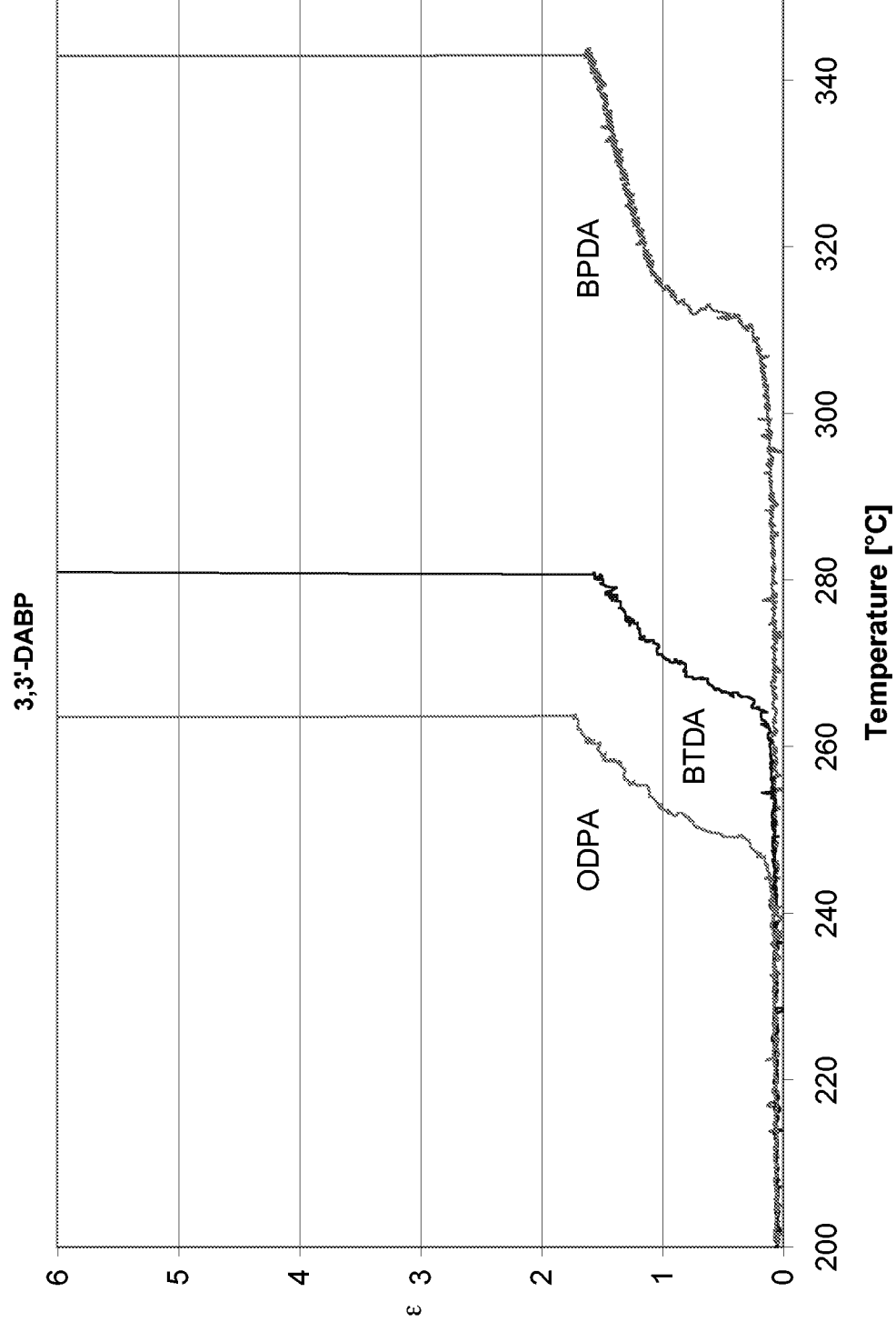Figure 4. TDA behavior of 3,4'-ODA-containing polyimides

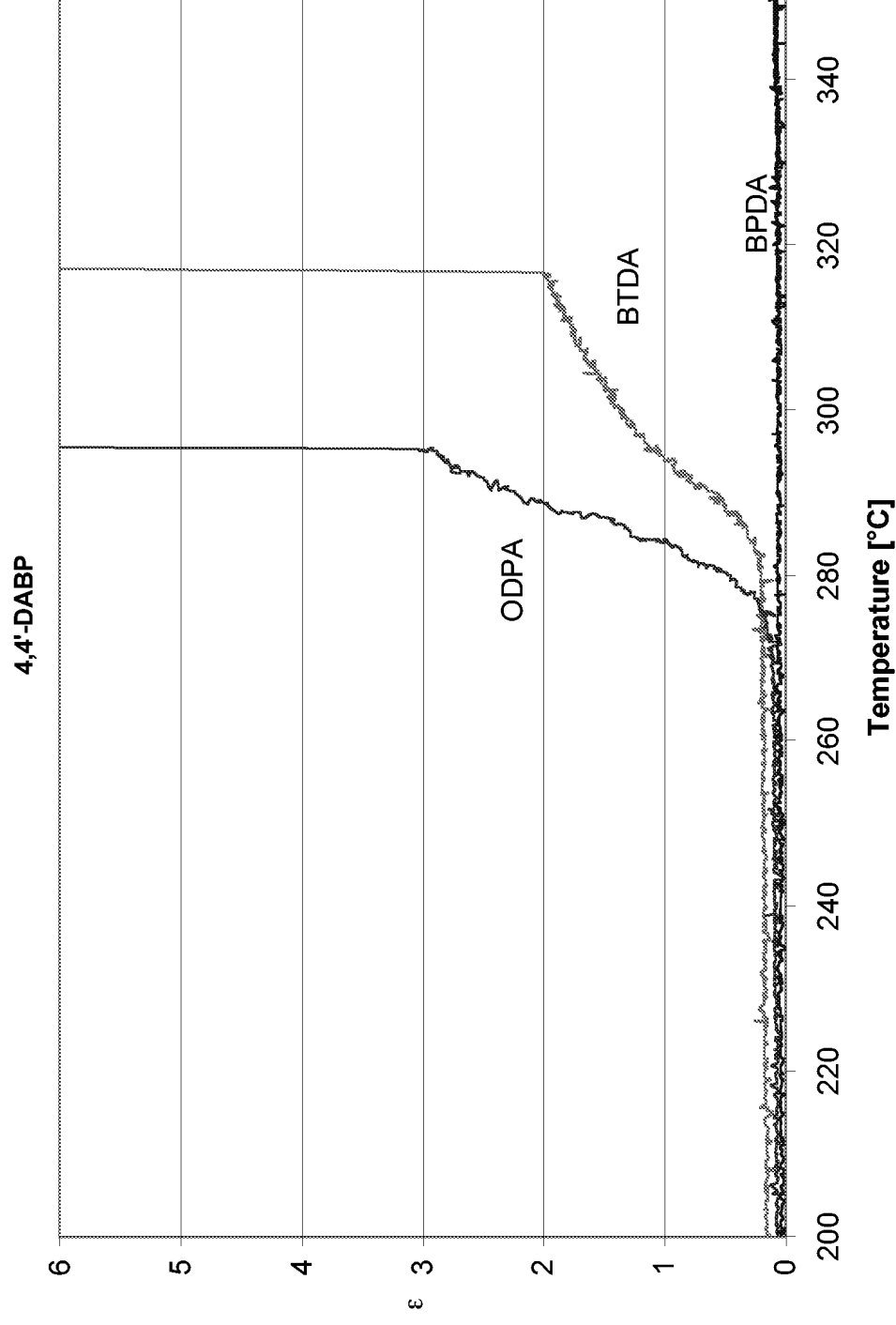Figure 5. TDA behavior of 3,3′-DABP-containing polyimides
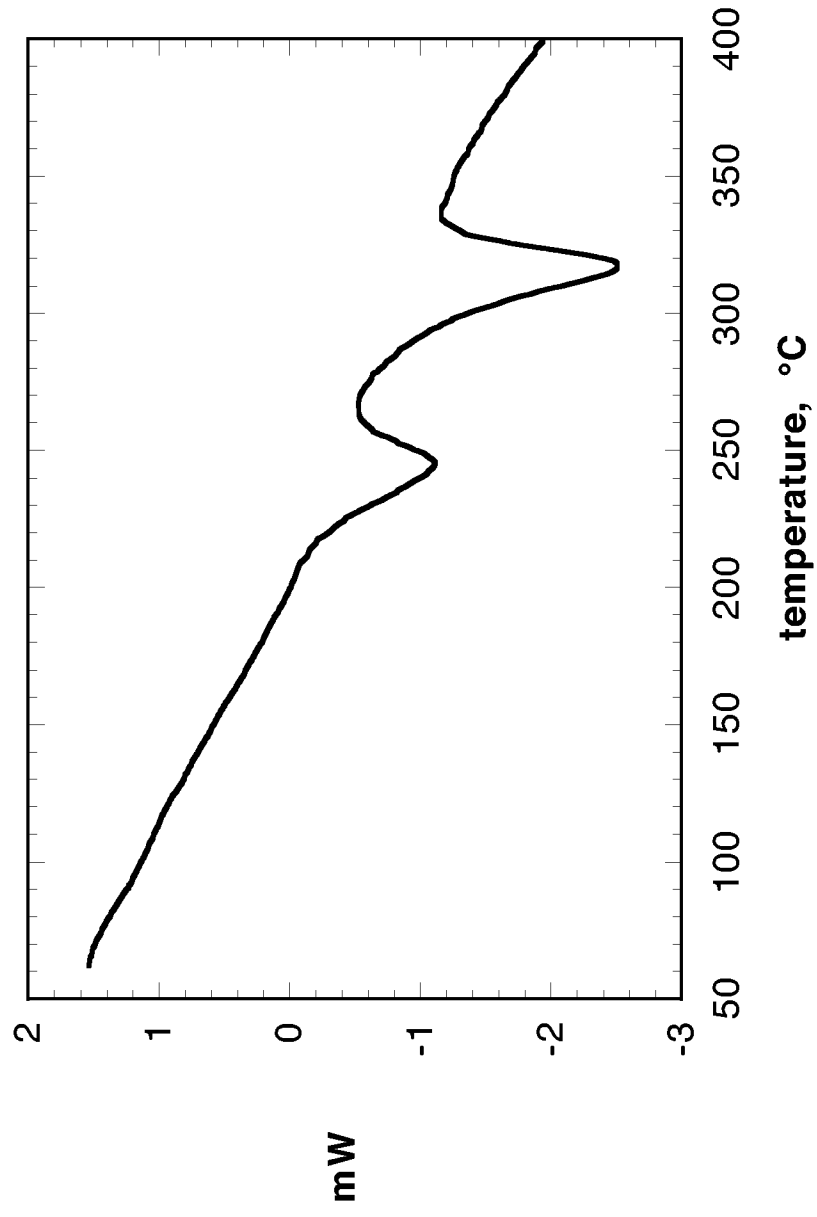
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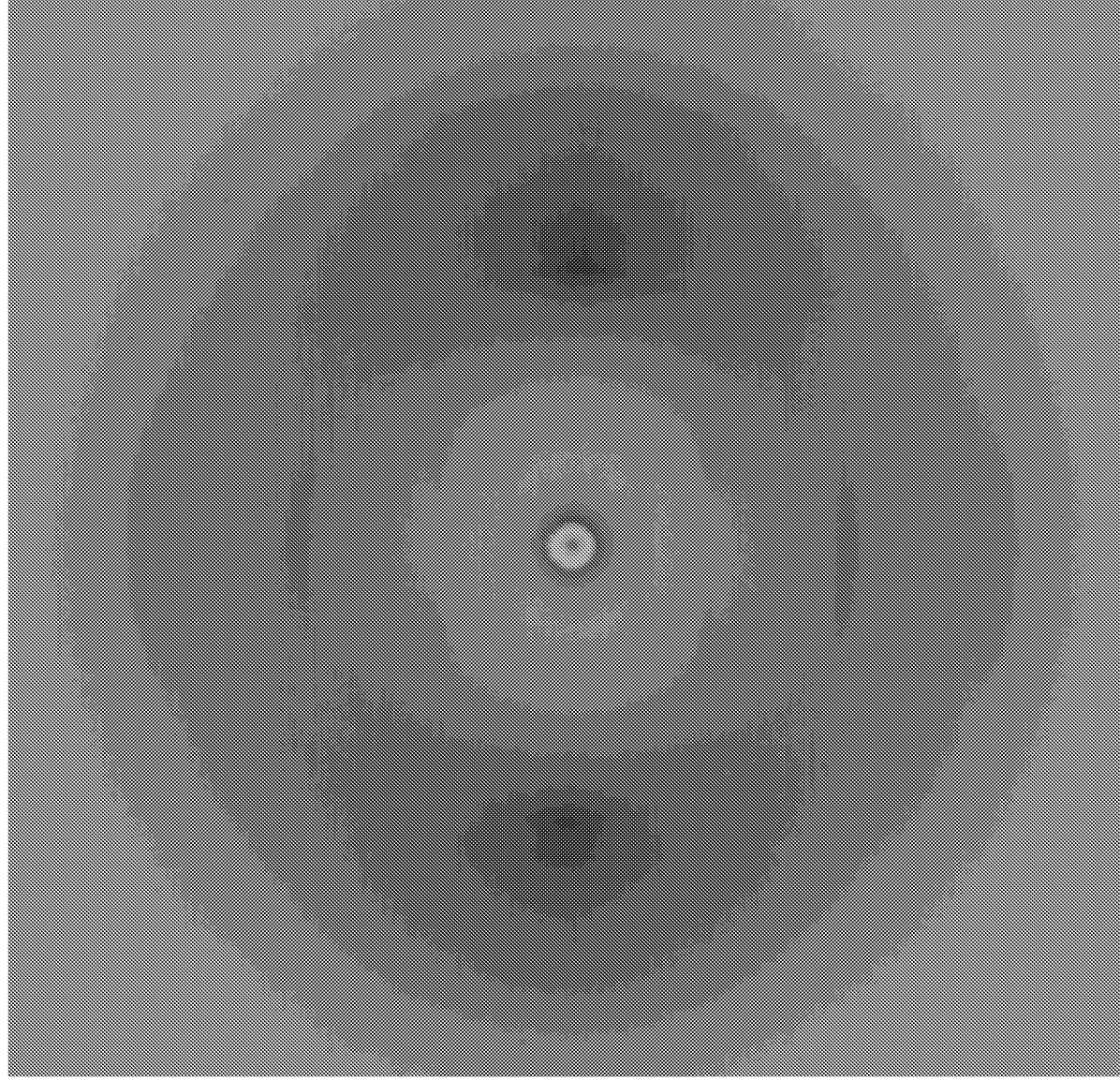
Figure 7. DSC of isothermally-stretched 3,4'-ODA/ODPA

Figure 8. Flat-plate X-ray photo of 5X-stretched 3,4'ODA/ODPA polyimide

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