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An Investigation of the Crystallinity of Kel-F, Viton, and Estane

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DEVELOPMENT DIVISION

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Normal Process Development
Endeavor No. 106

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ABSTRACT

Samples of Kel-F 800, Viton A and Estane 5702-F1 were annealed at 323 K and their crystallinity was tested by X-ray diffraction, thermal mechanical analysis and differential scanning calorimetry. After annealing for three months, all three samples exhibited some crystalline properties.

DISCUSSION

Materials such as Kel-F 800, Viton A and Estane 5702-F1 are used for high explosive binders and lot-to-lot variations in their mechanical strength have caused concern from time-to-time. Binder crystallinity has been recognized as a potential factor which may influence mechanical strength, but has not been fully explored in the past.

This investigation was initiated to determine if Kel-F, Viton and Estane exhibit some crystalline property that could be determined by X-ray diffraction. These materials would also be examined using thermal mechanical analysis and differential scanning calorimetry.

Samples of these binders were in the form of small chips or crumbs and it was necessary to form sheets before certain tests could be conducted. Initially sheets of Kel-F were made by dissolving the binder in a solvent such as acetone and then allow the solvent to slowly evaporate. Sheets of Kel-F were formed and after several weeks a thermal mechanical analysis (Fig. 1) was made on a small disk cut from the sheet. As the sample's temperature approached the glass transition ($\sim$ 300 K) the sample began to expand rapidly. This was caused by small bubbles formed by the residual solvent in the sample. Fig. 2 show photographs of a sample before and after heating. This method of preparing samples was not successful and was discontinued.

Samples of each of the three polymers were successfully prepared by heating the samples at 373 K in a confined container. The sample flowed together to form one piece.

Shortly after the samples were prepared they were analyzed by X-ray diffraction and found to be amorphous as expected (see Figs. 3, 4, and 5).

The samples were then annealed at 323 K for three months and then re-analyzed on the diffractometer and each sample showed some change. The Kel-F (Fig. 6) showed a considerable amount of crystallization over several diffraction peaks. There were fewer diffraction peaks and of less intensity with Viton, (Fig. 7) but crystallinity was still quite evident. Estane did not exhibit the normal diffraction peaks (Fig. 8) on the amorphous continuum, but the continuum itself became gaussian in appearance indicating that some internal ordering had taken place.

In addition to analysis by X-ray diffraction, thermal mechanical analysis (TMA) and differential scanning calorimeter runs (DSC-1) were made on each of the three binders.

TMA runs were made on two different samples of Kel-F 800, at high and low sensitivities and these results are shown in Figs 9 and 10, respectively. The higher sensitivity runs show a glass transition at about 293 K and a softening point at 355 K, and on reanalyzing this sample there was a considerable change in the thermogram. The softening occurred at the glass transition temperature.

Fig. 10 shows the TMA results at the lower sensitivity and there is only a very slight indication of a glass transition in the 290 to 300 K region. The softening point occurs near 355 K, and on rerunning the same sample there is some softening at the glass transition temperature followed by a softening point at 320 K. The amorphous sample has a softening point about 25 degrees lower than a crystalline sample.

The DSC-1 thermograms for a sample of Kel-F 800 are given in Fig. 11. The first run shows a shift in the baseline at 300 K and an endothermic transition at 360 K which are the glass transition and melting point, respectively. On rerunning the same sample the glass transition at 300 K is evident but a melt endotherm is not present indicating that the sample was then amorphous.

Fig. 12 shows the TMA thermograms for Viton A. The first run and the rerun are essentially the same. The DSC-1 results for Viton A are given in Fig. 13, and the first run shows a glass transition at 245 K and a small endotherm at 346 K which is the melting point. The second run shows the glass transition at 245 K superimposed on a small endotherm indicating that some crystallinity was formed as the sample cooled from the first run. However, there is no real evidence of the melting endotherm near 350 K.

The results for the Estane sample were somewhat similar to those of Kel-F. The first run in Fig. 14 shows a glass transition at 238 K with some penetration followed by a softening point near 323 K. On reheating the sample, there is no apparent change in the glass transition temperature but the softening point occurs at a much lower temperature (near 263 K). Amorphous Estane has a lower softening point temperature than the crystalline Estane.

The DSC-1 thermogram for Estane (Fig. 15) shows a shift in the baseline at 230 K and a very broad endotherm in the 310 to 340 K range which are the glass transition and the melting point endotherm, respectively. On rerunning the sample there was no endotherm in the 310 to 340 K range.

Some preliminary tests were made to determine if crystalline Kel-F could be detected in a 92.5/7.5 TATB/Kel-F matrix (RX-03-BB) using a Perkin Elmer DSC-2. Fig. 16 is a DSC-2 thermogram made with a 27 mg mixture of

TATB and crystalline Kel-F in the 92.5/7.5 ratio, and the Kel-F endotherm can be easily detected. A run was made on a formulation of RX-03-BB and no endotherm could be detected, indicating that the Kel-F was amorphous. Samples of the RX-03-BB were annealed for 5 days at 323 K and the thermogram is shown in Fig. 17. The Kel-F melt was easily detectable.

FUTURE WORK, CONCLUSIONS, COMMENTS

X-ray diffraction data and thermal analysis show that annealed samples of Kel-F 800, Viton A and Estane 5702-F1 display some crystallinity. The TMA results show that crystalline samples of Kel-F 800 and Estane 5702-F1 have a higher softening point temperature than amorphous samples. The TMA results for amorphous and crystalline Viton A were essentially identical.

Tests are planned to determine if annealing of samples of the plastic bonded explosives containing these binders will have an effect on the mechanical properties.

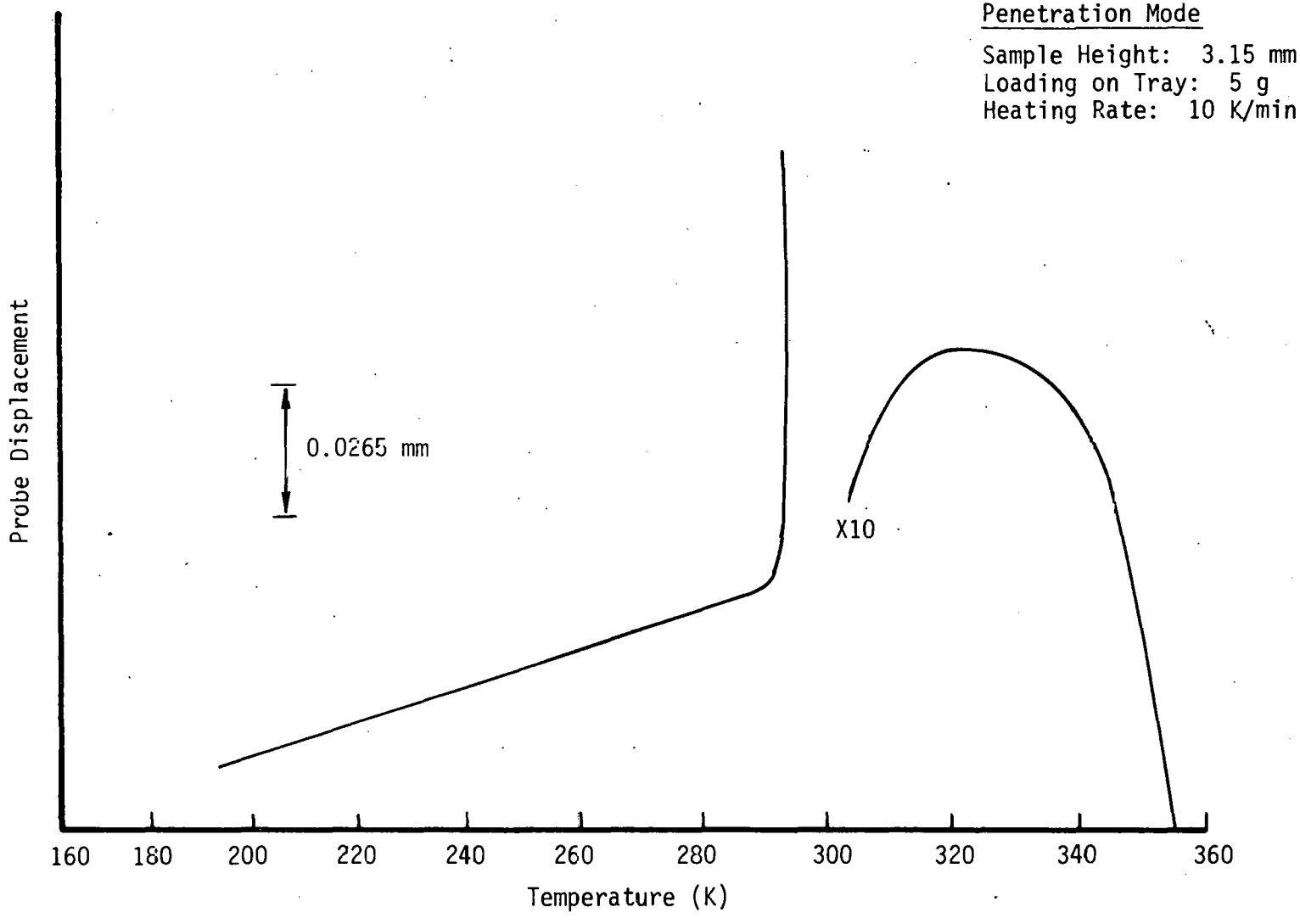
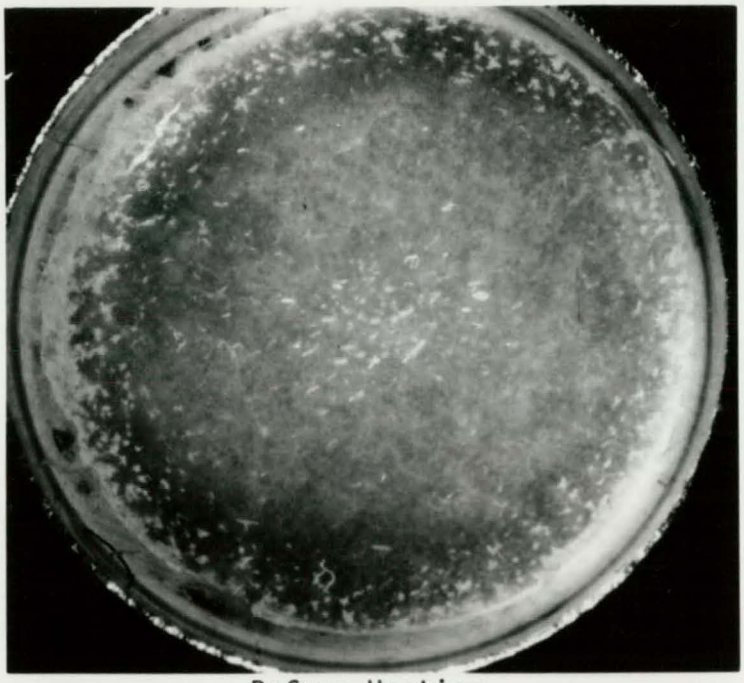
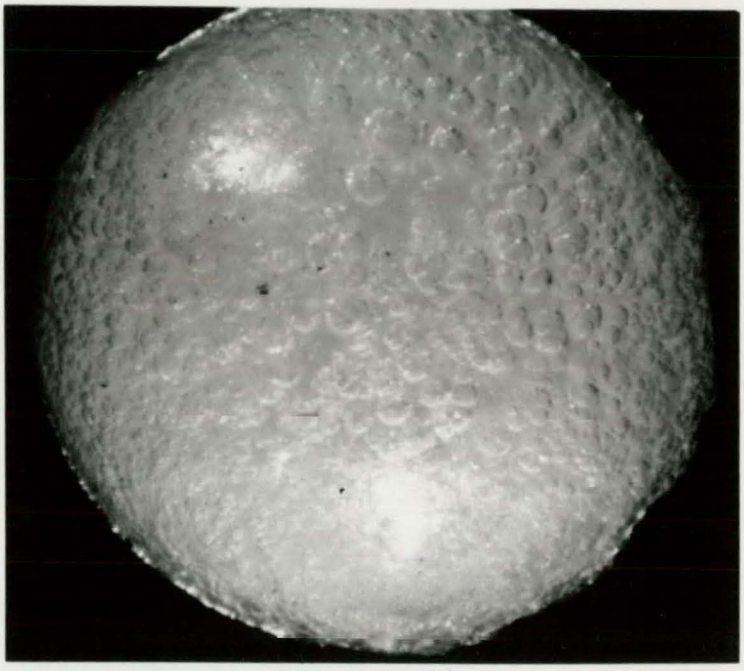


Fig. 1. TMA Thermogram of Kel-F 800 (Sample made by dissolving Kel-F 800 acetone to slowly evaporate)



Before Heating



After Heating

Fig. 2. Sample of Kel-F 800 Prepared by Dissolving in Acetone and Then Evaporating the Acetone Slowly

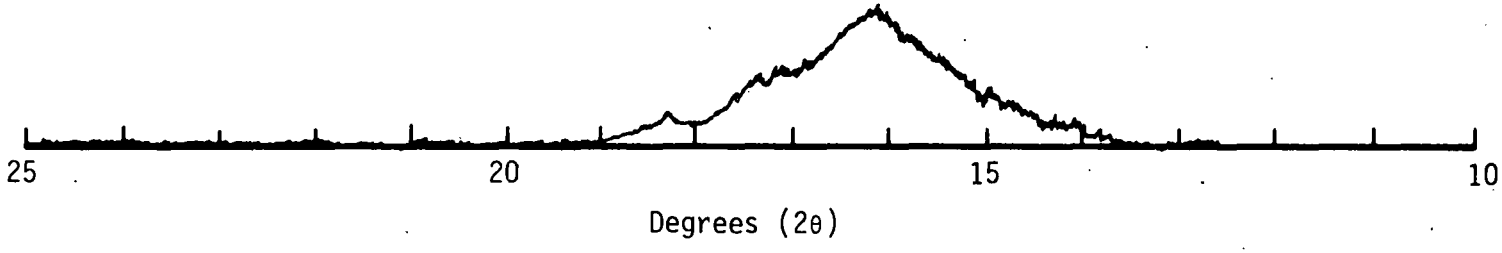


Fig. 3. X-Ray Diffraction Pattern for Kel-F 800 Before Annealing

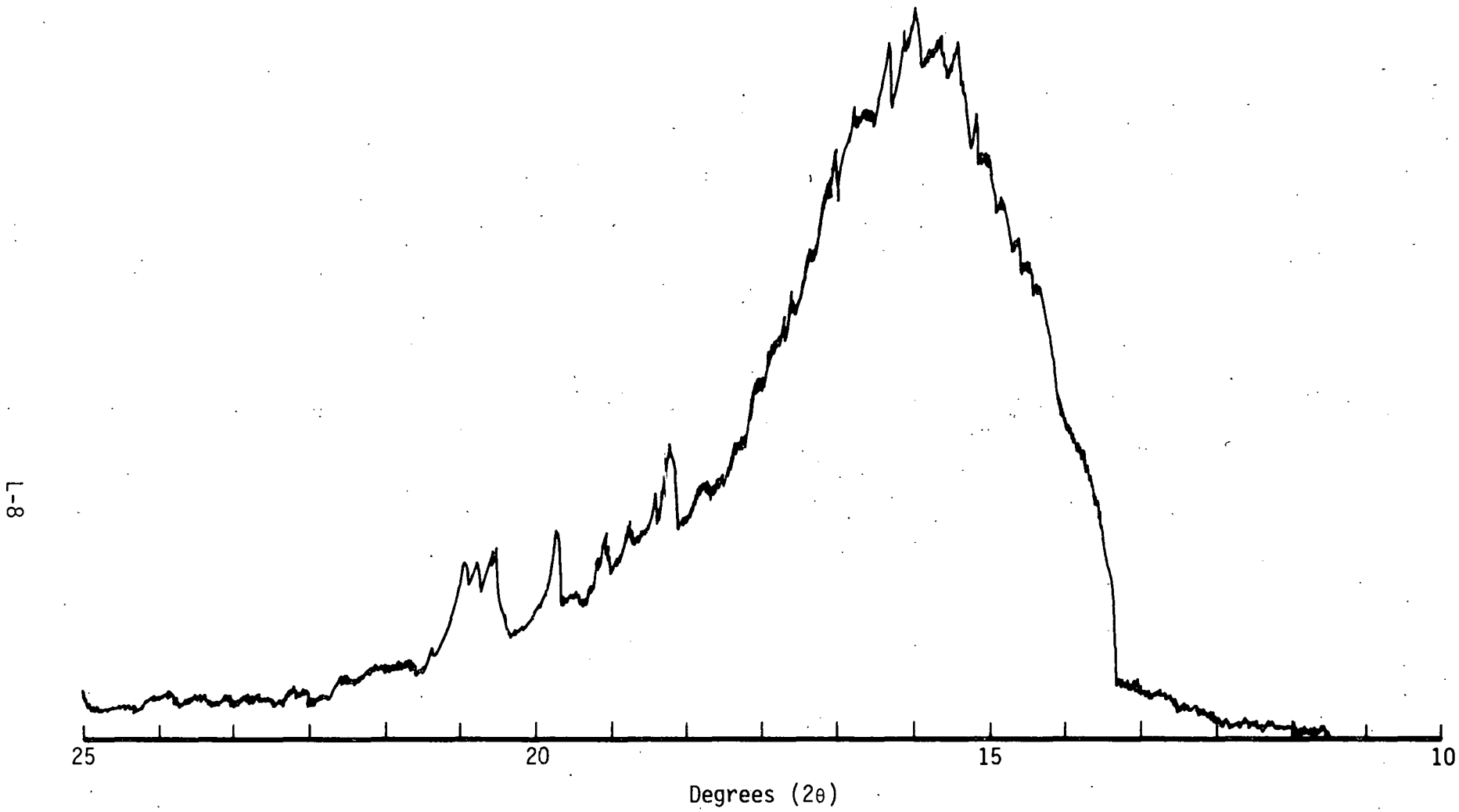


Fig. 4. X-Ray Difraction Pattern for Viton A Before Annealing

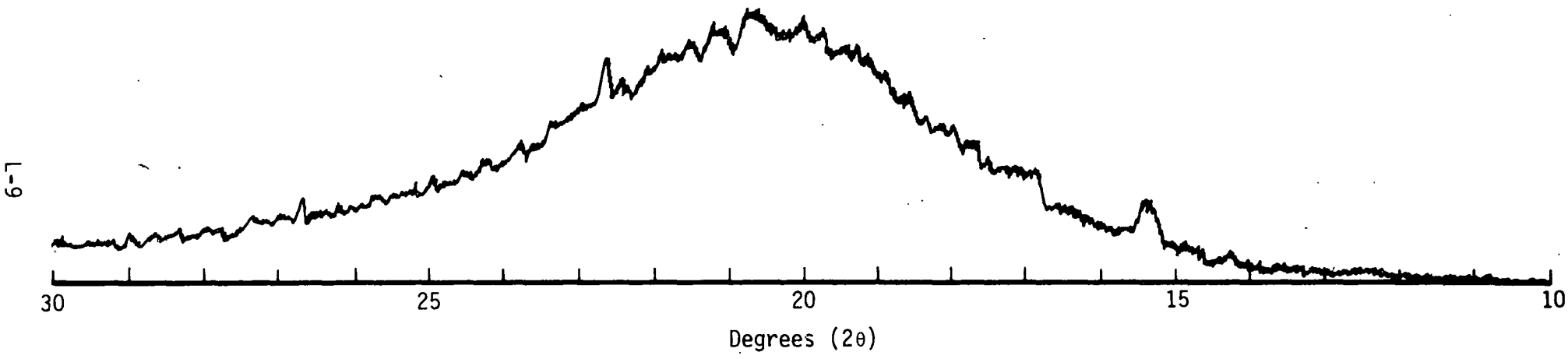


Fig. 5. X-Ray Diffraction Pattern for Estane 5702-F1 Before Annealing

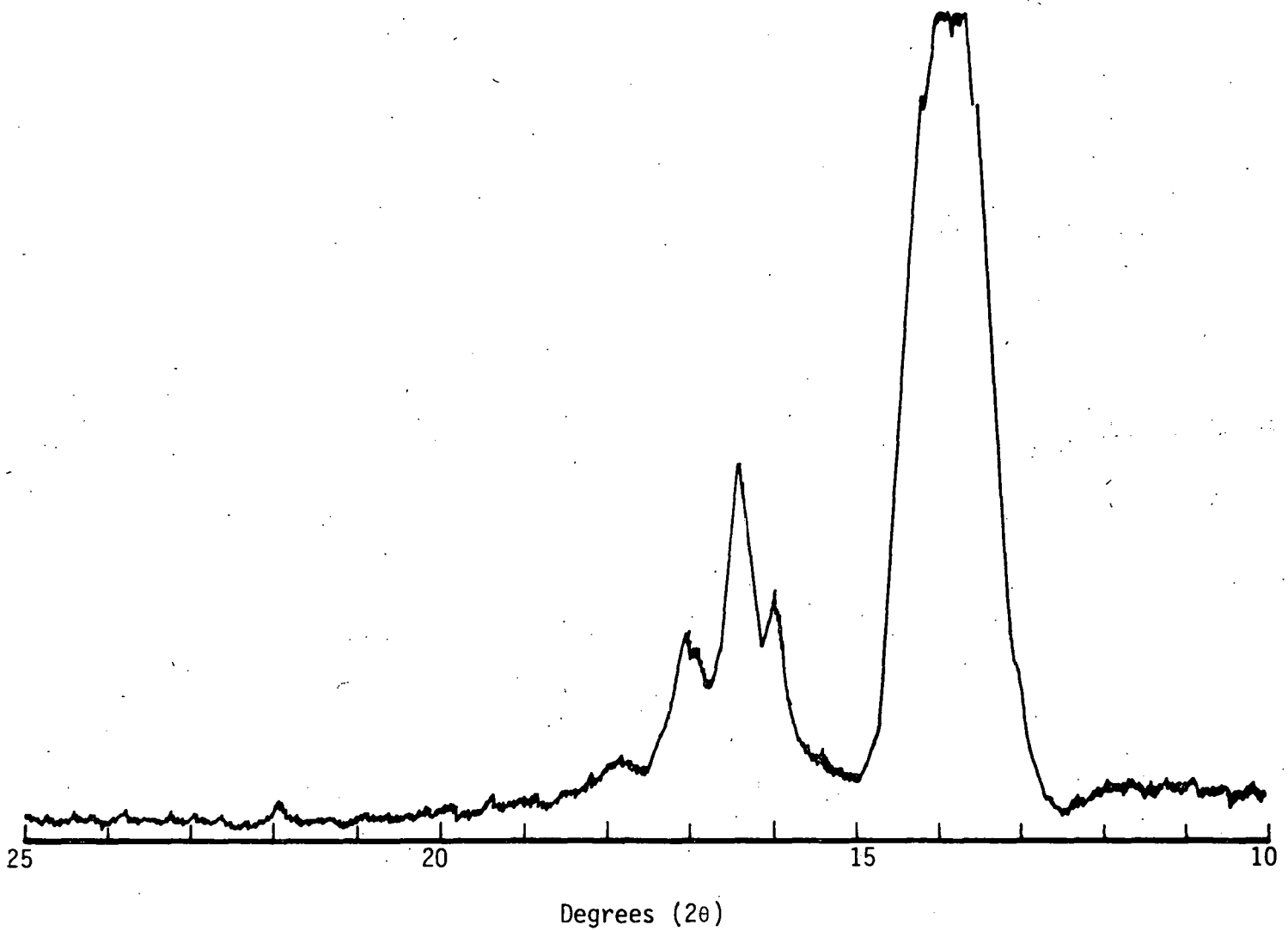


Fig. 6. X-Ray Diffraction Pattern for Kel-F 800 After Annealing

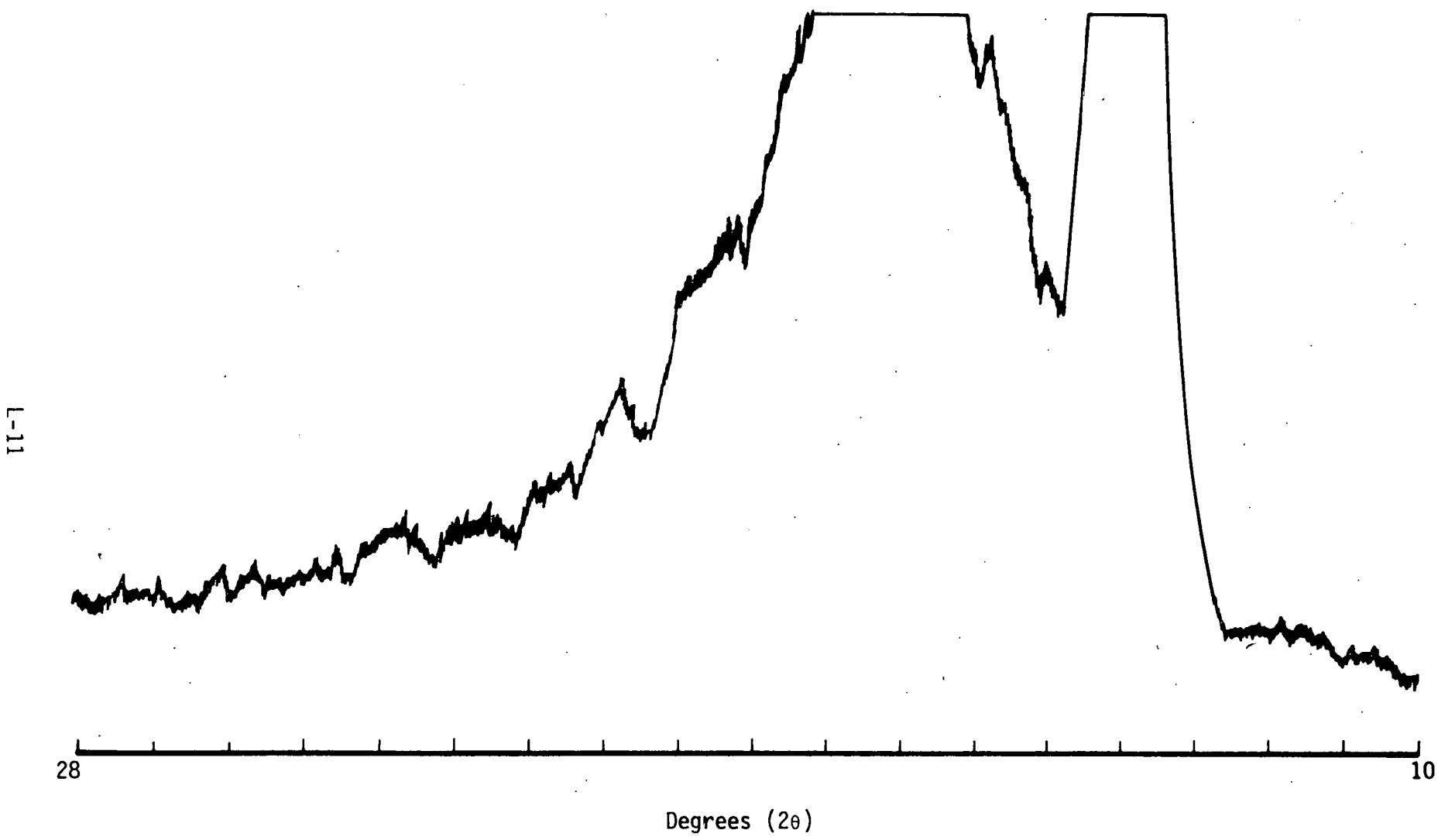


Fig. 7. X-Ray Diffraction Pattern for Viton A After Annealing

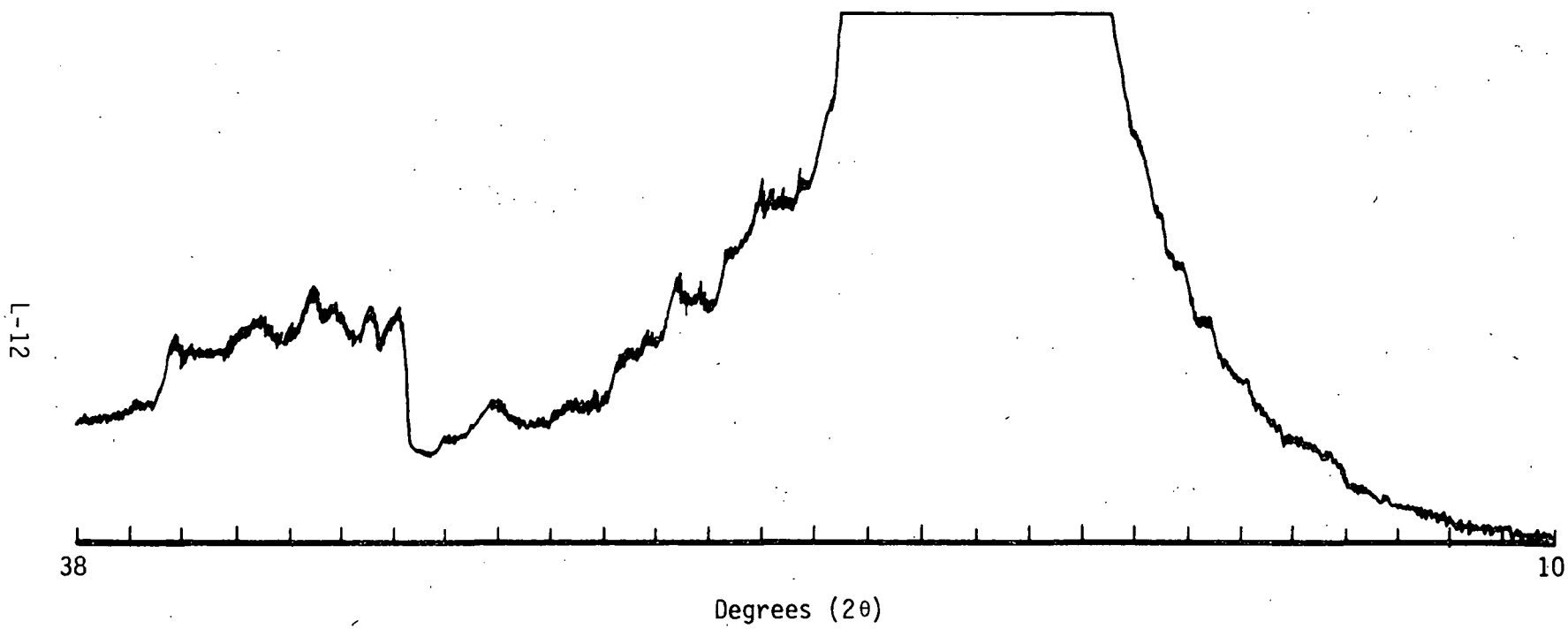


Fig. 8. X-Ray Diffraction Pattern for Estane 5702-F1 After Annealing

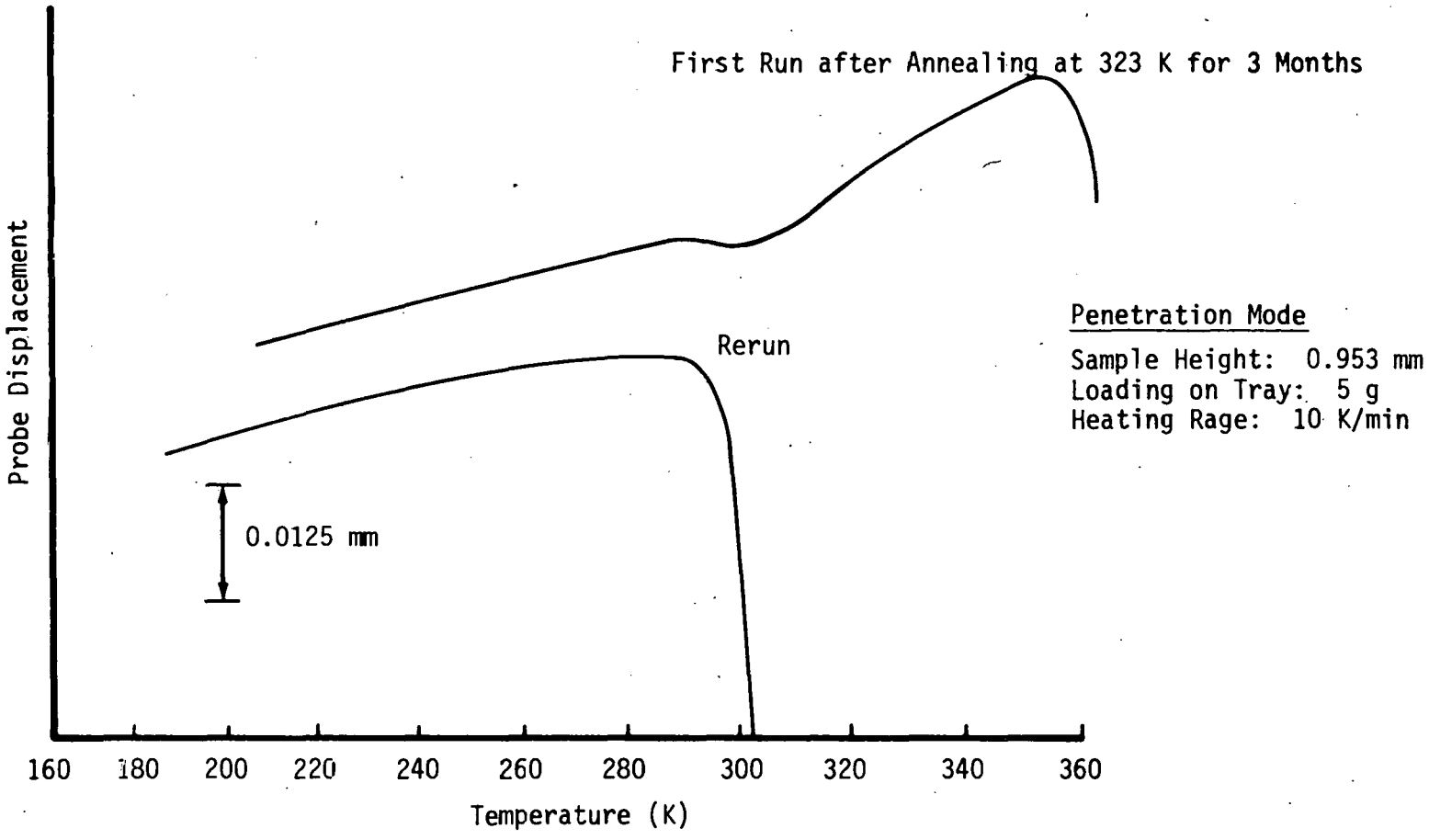


Fig. 9. TMA Thermogram of Kel-F 800 Maximum Sensitivity

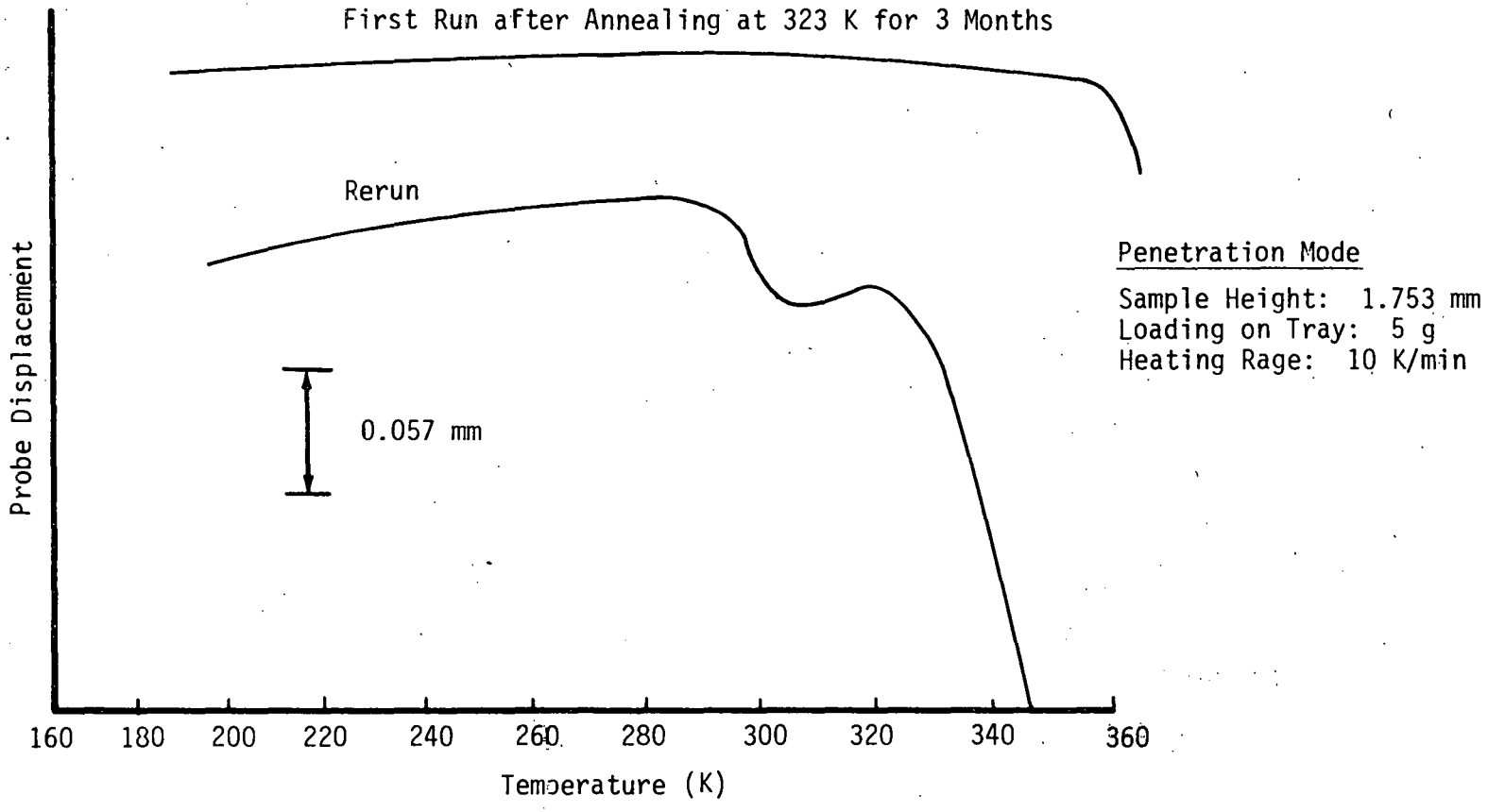


Fig. 10. TMA Thermograms of Kel-F 800

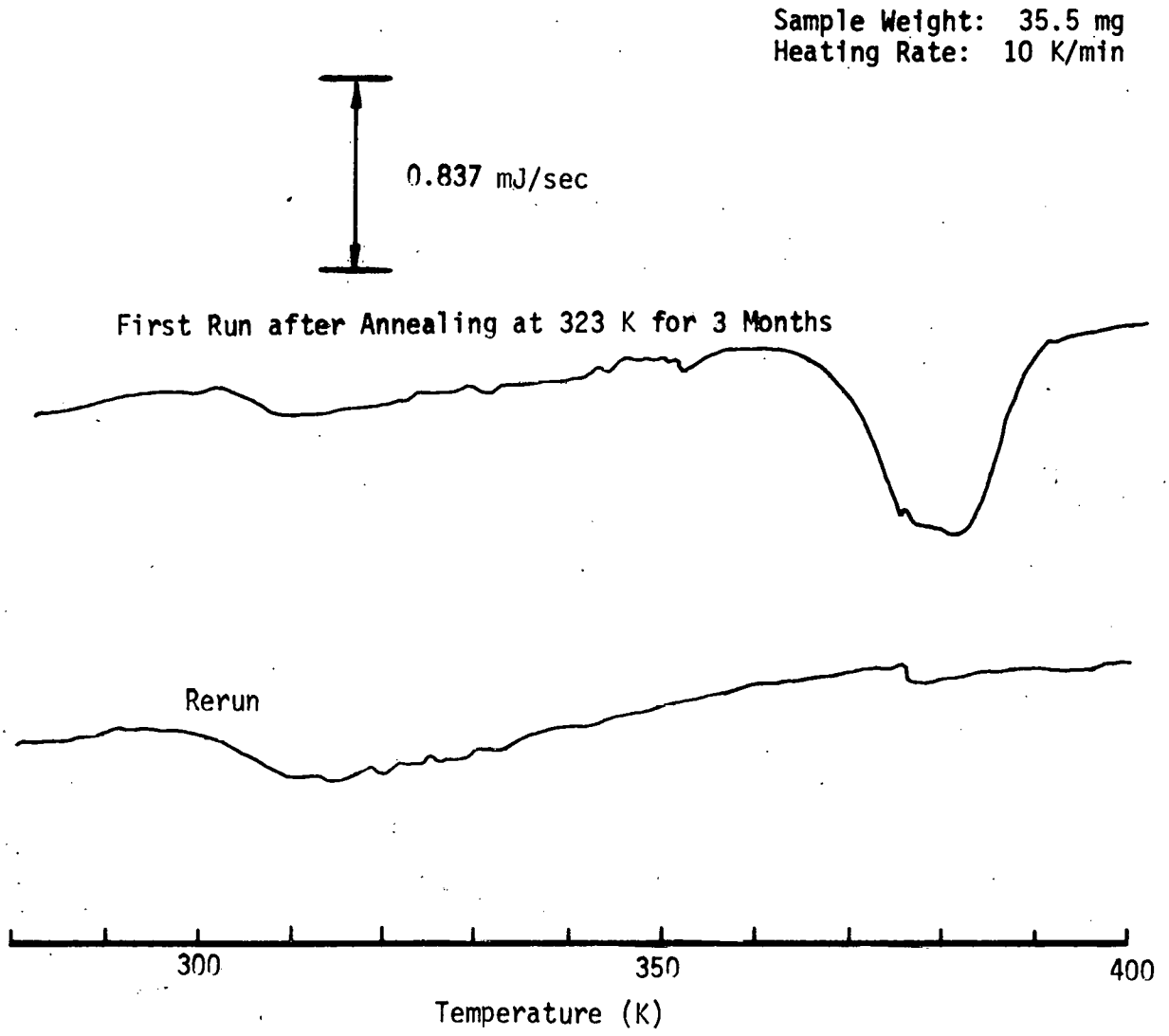


Fig. 11. DSC-1 Thermograms of Kel-F 800

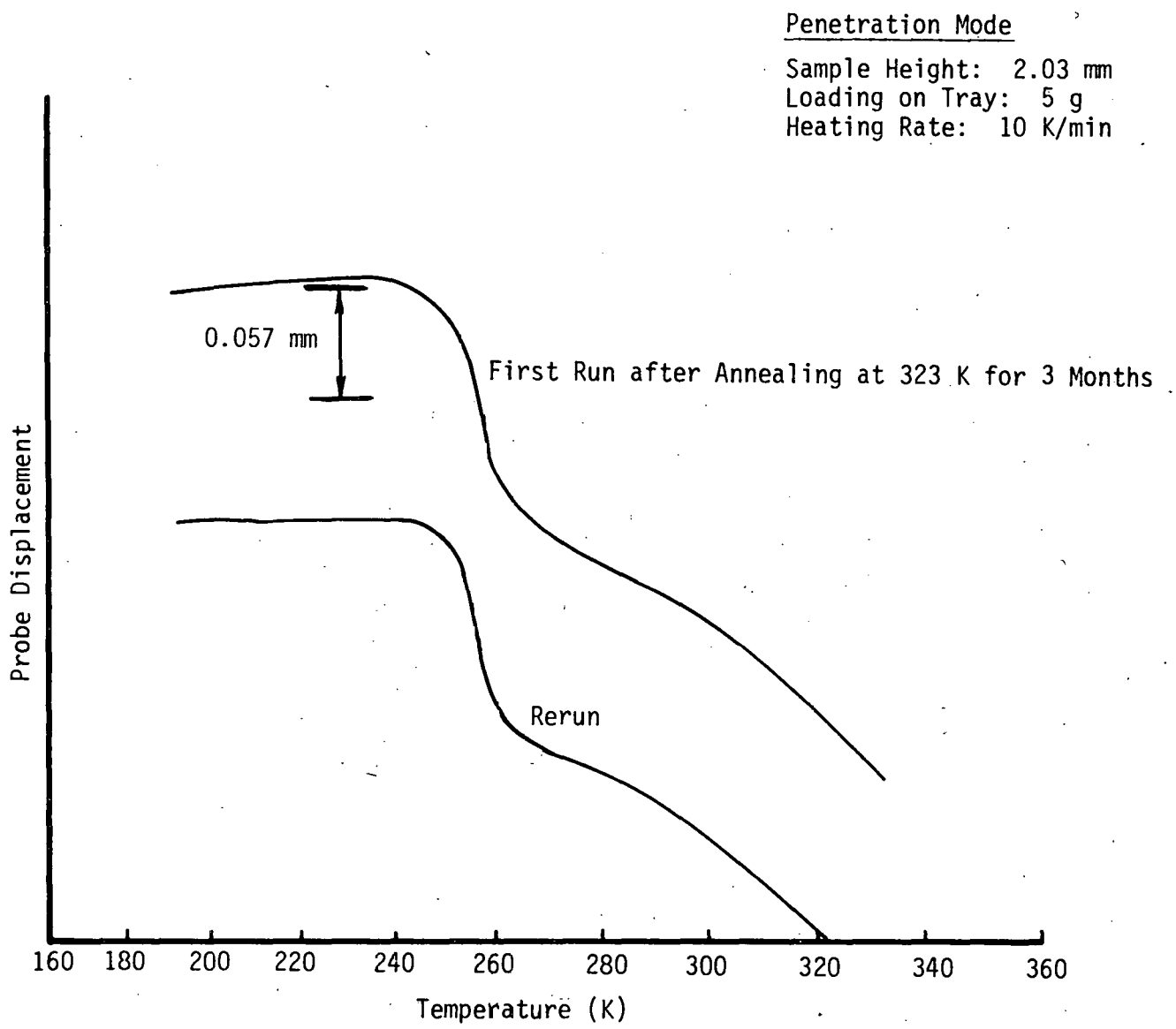


Fig. 12. TMA Thermogram of Viton A

Sample Weight: 21.8 mg
Heating Rate: 10 K/min

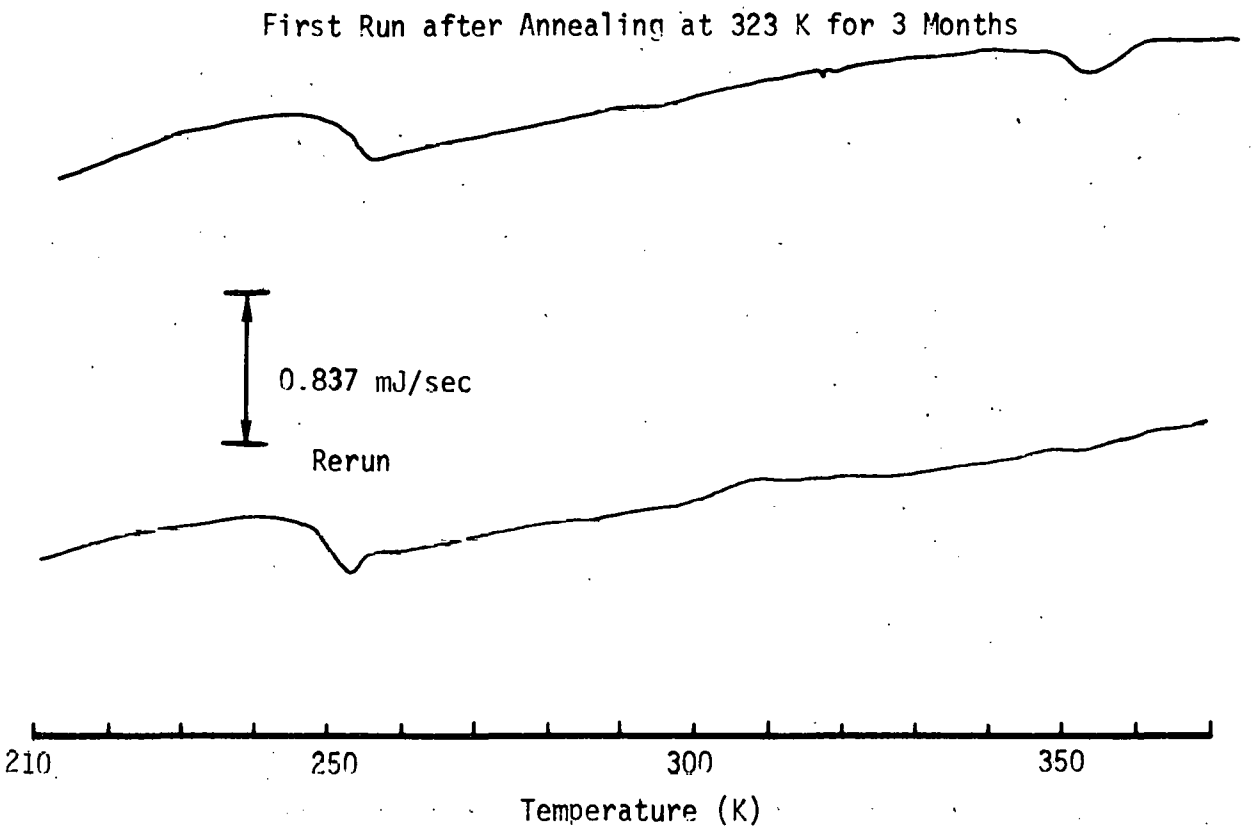


Fig. 13. DSC Thermogram of Viton A

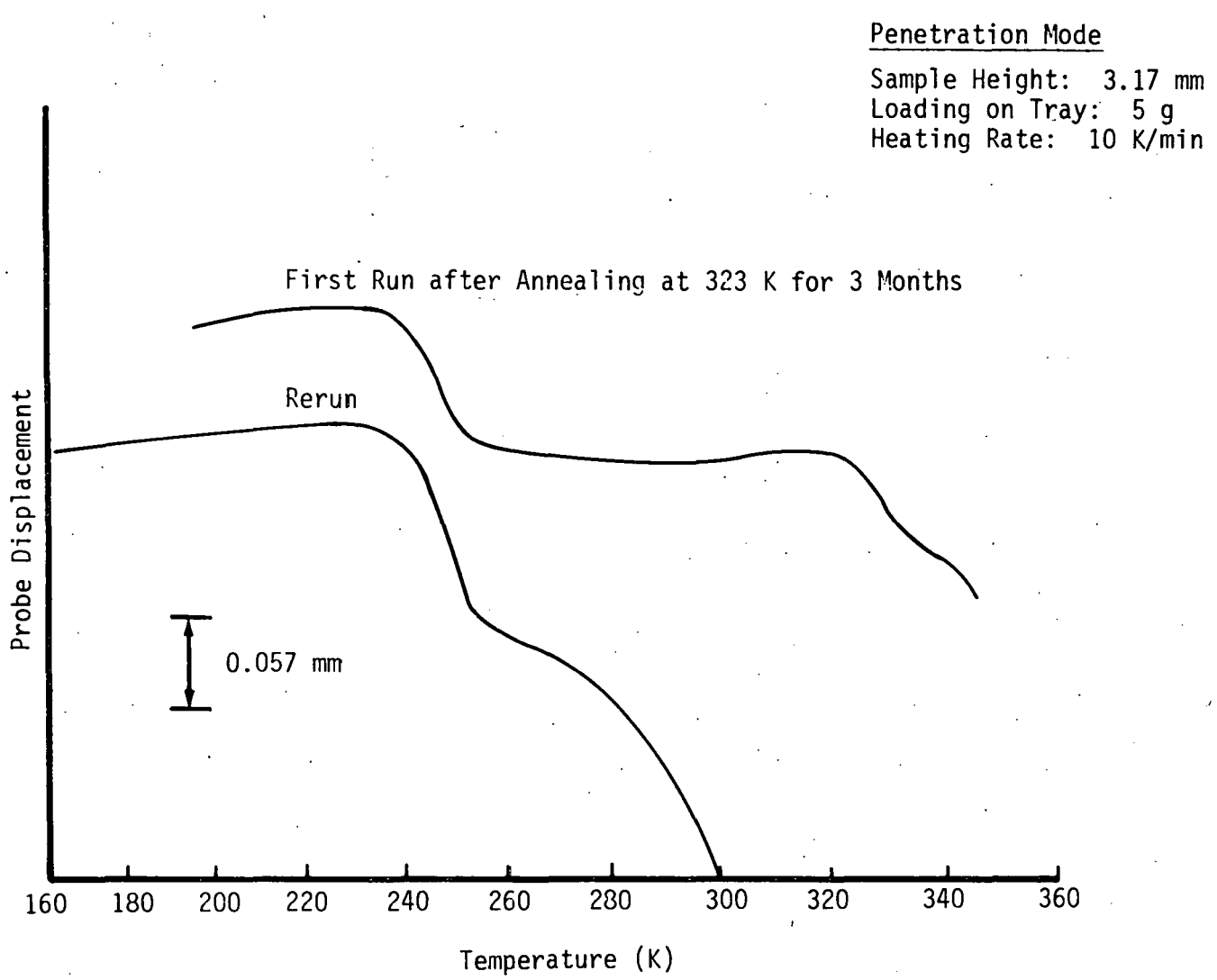


Fig. 14. TMA Thermogram of Estane

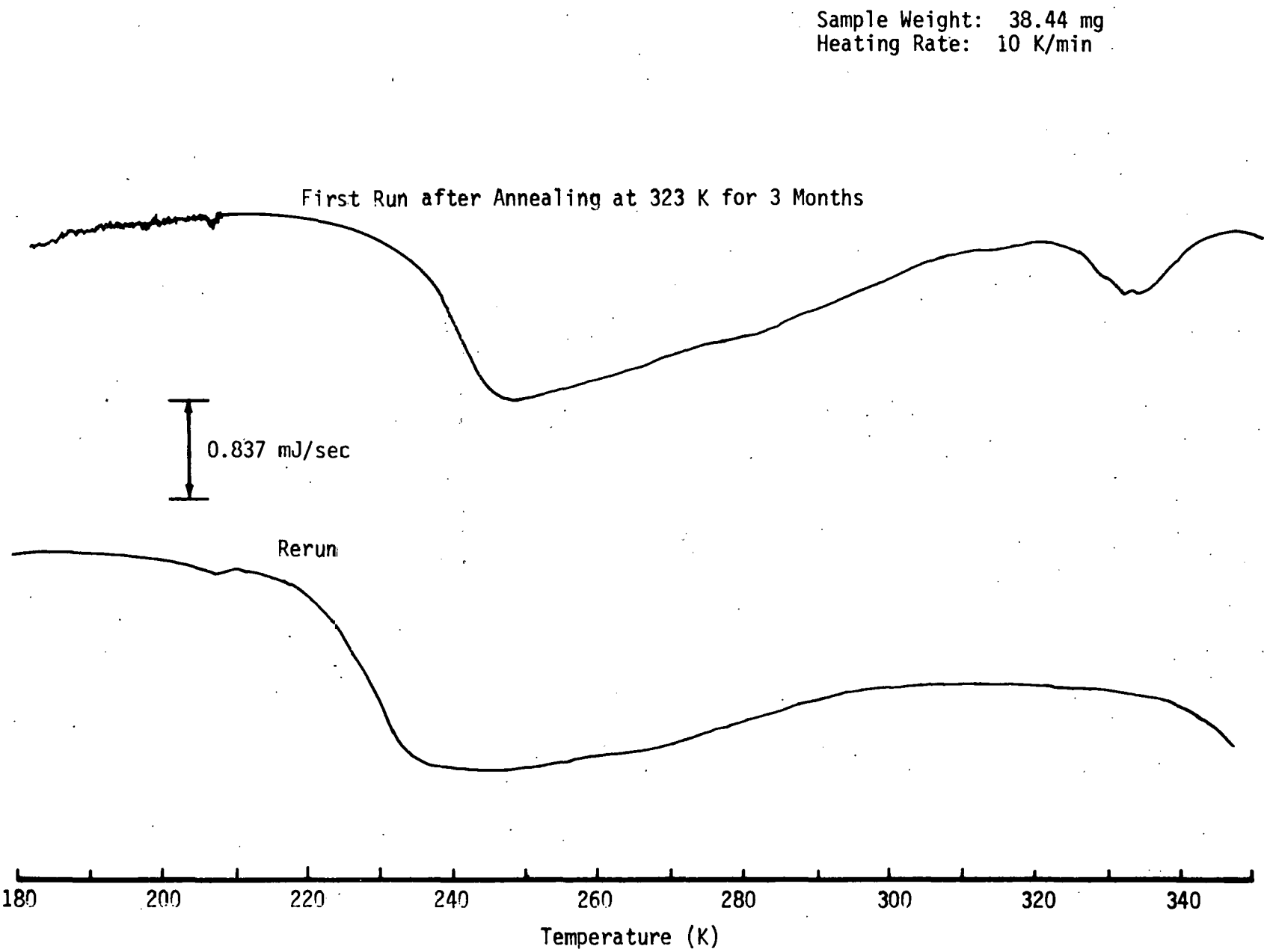


Fig. 15. DSC Thermogram of Estane

Heating Rate: 10 K/min
TATB: 24.98 mg
Kel-F: 2.02 mg
Total 27.00 mg

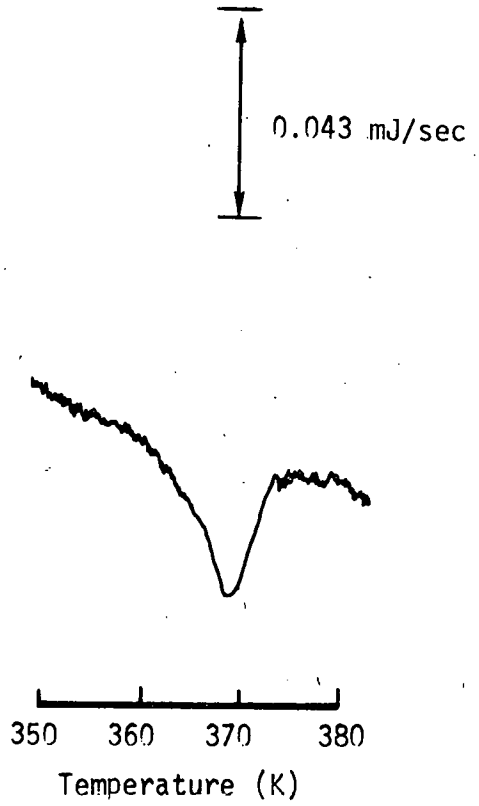


Fig. 16. DSC Thermogram of a Mixture of TATB and Crystalline Kel-F 800 (92.5/7.5)

Sample Weight: 24.13 mg
Heating Rate: 10 K/min

Annealed at 323 K for 5 Days

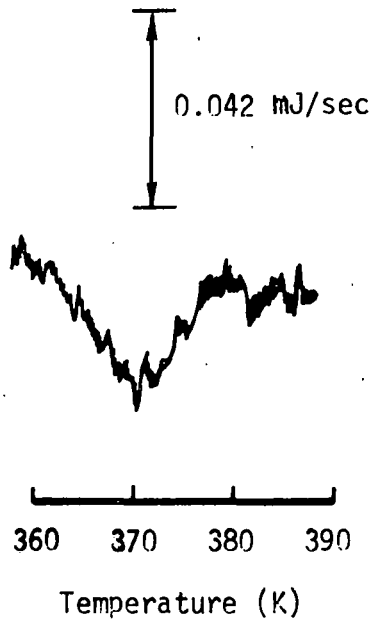


Fig. 17. DSC Thermogram of RX-03-BB (92.5/7.5 Mixture of TATB/Kel-F 800)