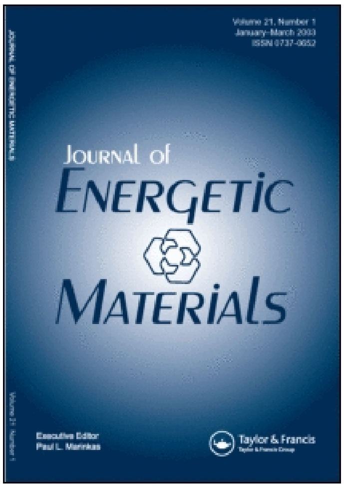

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The melting points of stable-form nitrate ester crystals

E. C. Braak[a]
[a] Hercules Aerospace Products Group Bacchus Works, Magna, Utah

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THE MELTING POINTS OF STABLE-FORM NITRATE ESTER CRYSTALS

E. C. Braak

Hercules Aerospace Products Group

Bacchus Works, Magna, Utah 84044-0098

ABSTRACT

The melting points of both neat and blended, stable-form, nitrate ester crystals were measured by differential scanning calorimetry and confirmed by visual observations. Most previously published data were obtained by freezing point measurements. These data tend to be low because of the strong tendency for nitrate esters to supercool, and also because of low-melting, labile, allotropic crystal formation by the pure materials.

Recognizing the limitations and scatter of the published data, this paper compiles in one readily accessible place, the measured melting points of stable-form crystals of five commonly used, neat nitrate esters and certain blends. It also describes the experimental techniques and equipment used to make the measurements.

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INTRODUCTION

The accurate measurement of the melting points of neat and blended nitrate esters is important because these materials are used as energetic plasticizers in explosives or high impulse rocket propellants which, in use, may be exposed to temperatures near or below their freezing points. Blending certain high and low melting nitrate esters produces eutectic mixtures that can be useful as low temperature plasticizers.

Kast[1] found that nitroglycerine (NG) may crystallize in two allotropic modifications, i.e., in both a labile and stable-form, of which only the first can be converted into the other. This conversion occurs readily, so that there is a monotropic allotropy. According to Kast, chemically pure NG is more difficult to crystallize, but it always crystallizes in the labile-form. Less pure NG, on the other hand, freezes more readily but mostly in the stable-form. On contact with a crystal of the stable-form, the labile-form converts to the stable-form immediately, or, without such contact, after a certain time.

The published freezing points for NG are very good because they have been carefully measured by numerous techniques for over 100 years. However, published melting/freezing points for four other, commonly available, reasonably energetic, nitrate esters with good stability are misleading. Like NG, each of these nitrate esters has at least two allotropic crystal forms. A lower melting labile-form and a higher melting stable-form, and the labile-forms also spontaneously convert to stable-forms. Thus, any nitrate ester plasticized explosive or propellant that has been embrittling for some time will contain the stable, higher freezing and melting crystal form because of this spontaneous conversion. Most of the published values were apparently measured on labile or mixed labile/stable crystal forms. These very low, published values make some of these nitrate esters seem more attractive as low temperature plasticizers than they really are.

EXPERIMENTAL

Materials

The NG, used for these measurements, was standard Hercules 99/1 production grade material prepared by the Biazzi process at the Bacchus Works, Magna, Utah. It contained 99.0 weight percent NG and 1.0 weight percent 2-nitrodiphenylamine (2NDPA) stabilizer. The other four nitrate esters were: trimethylolethane trinitrate (TMETN), diethylene glycol dinitrate (DEGDN), butanetriol trinitrate (BTTN), and triethylene glycol dinitrate (TEGDN). These were also standard production grade materials stabilized with 2NDPA, but they were purchased from the Trojan Division of the IMC Chemical Group, Inc. Spanish Fork, Utah. A small sample of each nitrate ester was "purified" by passage through a silica gel column in methylene chloride solution. This treatment removed the 2NDPA and all hydroxyl-containing impurities. These "pure" materials were used for melting point verification.

All samples were stored in antistatic-sprayed, 10 dram, soft polyethylene (PE), snap-top vials. The first 99/1 NG and TMETN samples froze spontaneously after only one or two -18° to -43°C temperature cycles. Crushed nitrate ester seed crystals were dropped onto the surface of prechilled specimens to provide instant nucleation sites and promote crystallization.

Most samples were encouraged to crystallize in every conceivable manner so their melting points could be measured. For example, all mixed ester samples were seeded with NG, BTTN, and TMETN crystals for consistency even though many of them were not composed of one or more of these materials. This was because TMETN crystals had successfully initiated NG crystallization after a power failure melted the first batch of NG crystals, and two months of -18° to -43°C cycling and seeding with graphite, dust, and ice had failed. Most of these seeded samples were temperature-cycled -18° to -43°C, reseeded if it seemed necessary, and eventually stored at whatever constant temperature produced the fastest crystallization. The mixed ester sample size was also increased from 2-3 g in 6 ml vials to 20-30 g in 30 ml (10 dram) vials when many of the smaller samples were not crystallizing. This was done because Noaum[2] had said that crystallization occurred more easily in larger samples. These larger samples did crystallize more rapidly, and eventually made possible the complete definition of the NG/BTTN melting point diagram.

Differential Scanning Calorimeter (DSC)

DSC thermograms proved to be the best method for measuring the melting points of the embrittled samples. Standard, open, preweighed, aluminum cups, (6.4 mm ID by 1.5 mm deep) were used for all samples. All samples and everything touching them were conditioned to -43°C. Neither cups nor samples were protected from water at any time during loading, and consequently, a thin, visible layer of frost coated everything.

All analyses were done with a Perkin-Elmer DSC, Model DSC-2, linked to a Perkin-Elmer Thermal Analysis Data Station. With this system, exotherms are represented going upward and endotherms downward. The instrument was calibrated on the high end to the Indium standard endotherm of 156.60°C. On the low end it agreed better than 2°C with both water (0°C) and 1,2 dichloroethane (-35.4°C) melting points. The DSC was covered with a plexiglass glove box containing a sample introduction chamber. This box was continuously flushed with dry nitrogen passed through mixed Type 4A and 13X molecular sieves in a Hydro-Purge II drying cartridge.

Each sample was scanned at 10°C/min from -110° to 50°C, then quickly recooled to -110°C, and rescanned. After rescanning, the cups were weighed, and the sample weights entered into the computer for the various enthalpy calculations. Samples were scanned twice to estimate their crystal contents. First scans generally showed a melt endotherm and varying, and sometimes quite large, glass transition (Tg) energies, while the rescans usually showed only large Tg energies; i.e., the rescanned samples were entirely amorphous. Now, since only amorphous (noncrystalline) materials have Tgs, the Tg energy measured in the first scan, divided by that of the second scan, yields a rough percentage of amorphous materials present during the first scan. Subtraction from 100 gives the crystal content. All Tgs were measured and reported as Tg 1/2s.

Visual Melting Point Observation

A stainless steel melting point block was made as shown in Figure 1. This block was chilled to a temperature below the anticipated melting point of the sample to be examined. The block slowly warmed in ambient air, and the melting of the sample (placed on a cover glass in the center of the block) was observed with a microscope. Light was reflected up through the hole in the bottom of the block.

The block was insulated with a snug, PE foam ring around the sides, and removable foam pads on the top and bottom. A desiccant collar was placed between the top of the block and the microscope. The microscope viewing lens fits into, and nearly fills the top of the collar. This collar prevents frost from obscuring the top cover glass. The warming rate of the block in ambient air, with all insulation in place, was 0.2°C/min, and with both top and bottom pads removed, 0.4°C/min.

A battery operated, electronic, Type K, thermocouple thermometer (Cole Parmer Model No. 8110-10), reading in 0.1°C was used for all melting point measurements. The instrument was zeroed periodically using a stirred, crushed-ice and water bath as reference.

DISCUSSION OF RESULTS

Melting points were measured because: (a) for pure compounds, melting and freezing points should theoretically be identical, (b) they are easier and more accurate to measure than freezing points because of the strong supercooling tendency of nitrate esters, (c) mixed nitrate esters freeze very slowly but melt quickly, (d) labile-form crystals tend to form during freezing point measurements, and (e) labile-form crystals require some time to spontaneously convert to their higher melting stable forms.

Neat Nitrate Esters

The crystals of both the 99/1 "as-received" and "purified" nitrate esters were generally transparent and had sharp, geometric angles. The visually observed start-of-melt point was taken as the first definite crystal movement or liquid flow, while the end-of-melt was the "all clear" point. As expected, the "purified" materials generally melted slightly (0.6° to 2.8°C) higher, and over smaller ranges. Higher melting, stable-form crystals were obtained initially in all cases except TEGDN. The visual start- and end-of-melt temperatures for two-week old "as-received" TEGDN crystals were -22.9° and -19.5°C respectively, but eight months later they had increased to -14.4° and -9.4°C respectively (Table 1).

TABLE 1. Visual Melting Points (°C) of Five Nitrate Esters

Nitrate Ester	Visual Observations			
	Purified[a]		As-Received	
	Start	End	Start	End
TMETN	15.7	17.1	12.9	16.1
NG	10.2	13.8	9.6	13.2
DEGDN	2.0	3.6	1.2	3.5
BTTN	-5.8	-3.2	-7.6	-2.8
TEGDN	-11.8 -25.4	-8.5 -19.0	-14.4 -22.9	-9.4 -19.5

a. All as-received 2NDPA and -OH cnt'g residues removed with silica gel column.

DSC thermograms of the crystallized 99/1 nitrate esters generally had straight baselines and sharp, single, major endotherms. There was little doubt about the major endotherm onset temperatures, and they fell between the visually observed start- and end-of-melt temperatures for the stable-form crystals (Figure 2). All samples used for DSC analysis were at least 6 months old, and had plenty of time to convert to their higher melting stable-forms.

Published melting or freezing points for the stable-forms of DEGDN and NG agreed within 1° and 2°C respectively with Hercules DSC endotherm onset temperatures (Table 2 and Figure 3). All of the other published data was measured on labile- or mixed labile/stable-form crystals except for the 51.0°C stable-form melting point for TMETN, which is obviously much too high and is probably a publishing error in °C/°F signs. It was probably meant to be 51.0°F (10.5°C), which then would be close to Hercules melting point of 13.0°C. Published labile-form freezing points for DEGDN and TEGDN agreed with Hercules DSC and visual observations respectively, and a published stable-form freezing point of -3.0°C for TMETN agreed with Hercules labile-form -3.8°C DSC melting point.

TABLE 2. Comparison of Visual and DSC Melting Points (°C) of Five As-Received Nitrate Esters with Published Data

Nitrate Ester	Visual Observations		DSC Major Endotherm Onset	Published Data[b]	
	Start	End		Stable	Labile
TMETN	12.9	16.1	13.0 -3.8[a]	(-3.0)[T,K,O],51.0[U]	(-15.0[M], -17.0[K])
NG	9.6	13.2	10.9	(13.2)[M,K,O]	(2.2)[M,K]
DEGDN	1.2	3.5	3.3 -10.5[a]	2.0[U,M,T,K]	-10.9[U,M,K], -11.3[O]
BTTN	-7.6	-2.8	-5.9	(-11.3)[C]	(-27.0)[M,T]
TEGDN	-14.4 -22.9	-9.4 -19.5	-11.6 --		(-23.0)[T], (-19.0)[K]

a. Labile crystals formed during immediate rescan of melted original samples.
b. (Freezing points in brackets); melting points without brackets.

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Various water blanks were run to help with DSC thermogram interpretation because water could not be excluded during sample loading. Water generally proved not to be a serious problem. No scan was ever repeated specifically because water had interfered.

Second run thermograms showed that TMETN and DEGDN freeze so quickly and easily that fully melted, first run samples recrystallized into their labile-forms from the amorphous, super-cooled state, as evidenced by their large crystallization exotherms. Figure 4 shows typical first and second run thermograms for TMETN. The melt endotherm onset temperatures that followed these exotherms agreed better than 1°C with published stable or labile-form melting or freezing points for these materials (Table 2).

The crystal contents of the five, neat, 99/1 nitrate esters were obtained by using the first and second run Tg energies as described in the experimental section. Thus, TEGDN, DEGDN, and TMETN were essentially 100% crystallized, while NG and BTTN were only 91% and 84% crystallized respectively (Table 3). This is consistent with the fact that BTTN is inherently quite difficult to crystallize because of its asymmetry, and probably also because of mixed optical isomers in the butane triol starting material, which yield optically-isomerized BTTN.

Mixed Nitrate Esters

Mixed nitrate ester crystals were translucent and had no sharp, geometric angles. Many of the visually observed melting samples had well-defined start- and end-of-melt points. The purer the sample (e.g., 100% NG or BTTN), the closer these points were; the less pure the samples, the further apart. For example, the 70:30 NG/BTTN mixtures start- and end-of-melt temperatures are -9.4° and 6.7°C respectively; a 16.1°C range (Figure 5). Changing the BTTN concentration produced a start-of-melt eutectic of -20.6°C for the 40:60 NG/BTTN mixture.

Several crystallized, mixed nitrate ester samples held for a week at -12.2°C, part way between their start- and end-of-melt temperatures, only partially melted. Specifically, these were the 60:40 and 30:70 NG/BTTN mixtures in Figure 5. These

TABLE 3. DSC Scans of Five As-Received Nitrate Esters

Nitrate Ester	Major Endotherm Onset (°C)	Glass Transition $Tg_{1/2}$				Crystal Content (%)	Visual Start-of-Melt (°C)
		First Run		Rerun			
		(°C)	(Cal/g)	(°C)	(Cal/g)		
TMETN	13.0 -3.8^a	(No Tg)		-65.6	0.173	100.0	12.9
NG	10.9	-61.5	0.021	-72.6	0.231	90.9	9.6
DEGDN	3.3 -10.5^a	(No Tg)		-86.9	0.239	100.0	1.2
BTTN	-5.9	-68.0	0.039	-68.5	0.246	84.2	-7.6
TEGDN	-11.6	(No Tg)		-80.2	0.257	100.0	-14.4

a. Labile crystals formed during immediate rescan of melted original samples.

partially melted samples were partly clear transparent liquid and partly translucent crystals. Thus, the visually observed broad ranges between start- and end-of-melt are real, and the end-of-melt temperature is the potential start-of-freezing temperature.

The baselines of the DSC scans of many of the NG/BTTN mixtures were not as unequivocal as for the neat nitrate esters; however, within the extremes of the possible baseline positions, the major endotherm onset temperatures shifted less than ± 2°C. These major endotherm onset temperatures agreed ± 3°C with visually observed start-of-melt temperatures except for the 80:20 mixture, which was 7.5°C higher (Table 4 and Figure 6).

Crystallized mixtures of TMETN and BTTN have reasonably clean, generally unambiguous, major endotherm onset temperatures. Generally, the endotherms were broad with a gradual slope from onset to minimum. The DSC melting point eutectic curve for TMETN/BTTN (Figure 7) was similar to that for the NG/BTTN system (Figure 6). However, initially many of the mixtures crystallized in labile-forms. Seventy four days after seeding, the DSC melting point of the 90:10 TMETN/BTTN mixture was -20.8°C, and 26 days later it had increased to 3.1°C. The crystal content of

TABLE 4. DSC Scans of NG/BTTN Mixtures

Plasticizer Ratio	Major Endo Onset Temp (°C)	Glass Transition $Tg_{1/2}$				Crystal Content (%)	Visual Start-of-Melt (°C)
		First Run		Rerun			
NG/BTTN		(°C)	(Cal/g)	(°C)	(Cal/g)		
100:0	10.9	-61.5	0.021	-72.6	0.231	90.9	9.6
90:10	3.9	-72.9	0.039	-73.6	0.214	81.8	2.5
80:20	1.6	-69.7	0.035	-71.5	0.191	81.7	-5.9
70:30	-6.0	-71.7	0.128	-71.9	0.207	38.2	-9.4
70:30	-8.8	-72.1	0.101	-72.1	0.187	46.0	
60:40	-17.5	-70.1	0.047	-70.9	0.191	75.1[a]	-17.0
40:60	-22.3	-70.3	0.149	-69.8	0.192	22.4	-20.7
20:80	-16.7	-69.9	0.089	-69.1	0.230	61.3	-14.8
0:100	-5.9	-68.0	0.039	-68.5	0.246	84.2	-7.6

a. Unexplainably high crystal content.

the two samples was 74% and 77% respectively. This behavior indicates a dramatic labile/stable crystal transformation. Visual melting point observations for the 90:10 through 70:30 mixtures, made weeks or months before the DSC scans, also reflect this (Table 5). Generally the crystal contents of both of the mixed nitrate ester systems decreased as the more difficult-to-freeze eutectic mixtures were approached from either side (Tables 4 and 5).

CONCLUSIONS

Most published melting and freezing points for five commonly used nitrate esters were measured on low-melting labile or mixed labile and stable-form crystals. In several cases (specifically neat TEGDN and 90:10 TMETN/BTTN) dramatic increases in measured melting points with time demonstrated the reality of spontaneous labile- to stable-form conversions. Stable-form crystal melting points for these five

TABLE 5. DSC Scans of TMETN/BTTN Mixtures

Plasticizer Ratio	Major Endo Onset Temp (°C)	Glass Transition $Tg_{1/2}$				Crystal Content (%)	Visual Start-of-Melt (°C)
TMETN/ BTTN		First Run		Rerun			
		(°C)	(Cal/g)	(°C)	(Cal/g)		
100:0	13.0	(No Tg)		-65.6	0.173	100.0	12.9
90:10	-20.8	-67.1	0.064	-66.4	0.243	73.7	-18.3
90:10	3.1	-66.9	0.037	-66.9	0.160	76.9	
80:20	-11.5	-66.9	0.053	-65.8	0.184	71.2	-19.3
80:20	-9.6	-67.0	0.054	-65.8	0.170	68.3	
70:30	-16.5	-68.3	0.096	-66.9	0.198	51.5	-19.8
70:30	-13.6	67.2	0.146	-66.9	0.211	30.8	
60:40	-18.0	-67.9	0.024	-67.3	0.176	86.4[a]	-19.2
0:100	-5.9	-68.0	0.039	-68.5	0.246	84.2	-7.6

a. Unexplainably high crystal content.

nitrate esters and various blends were measured, and the 40:60 NG/BTTN eutectic mixture identified.

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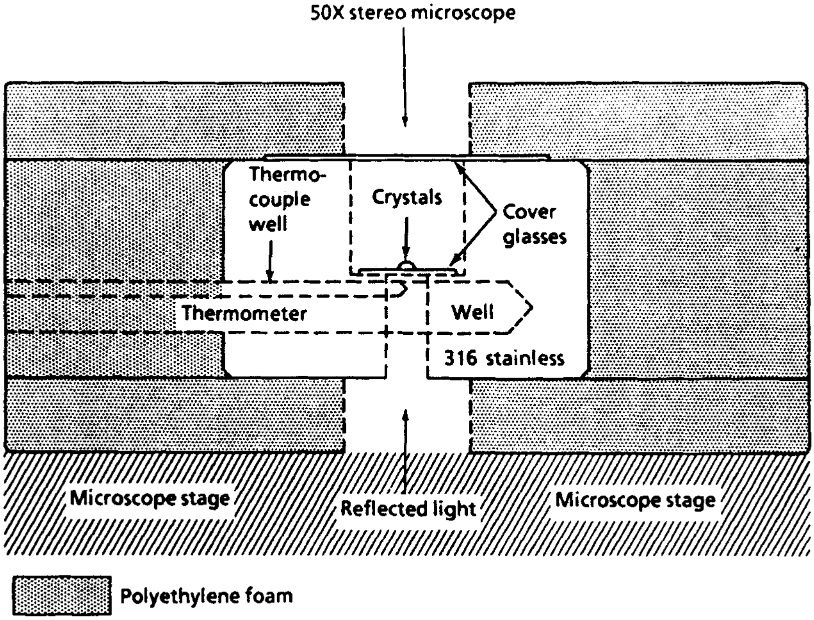

FIGURE 1. Stainless Steel Melting Point Block

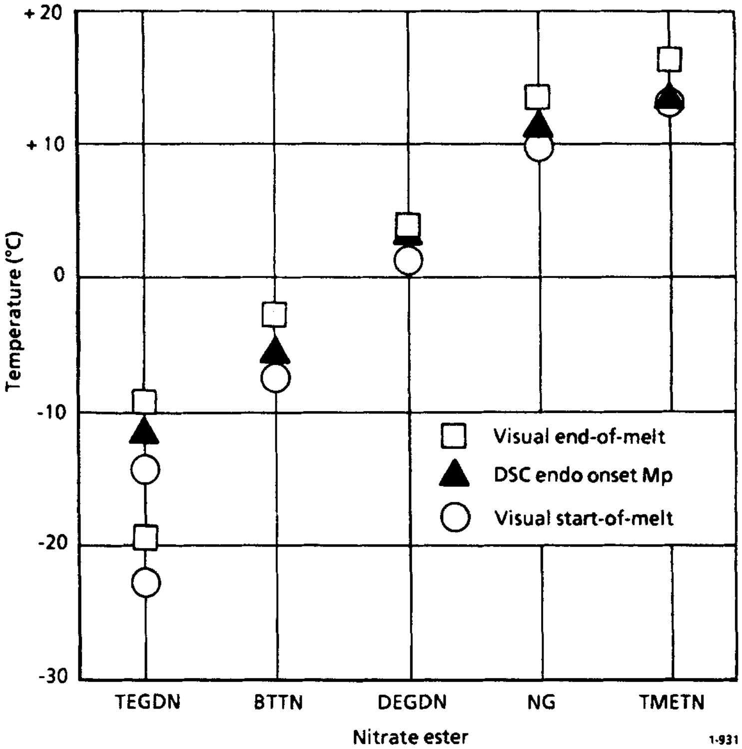

FIGURE 2. DSC Major Endotherm Onset Temperatures for Neat Nitrate Esters Agree with Visual Melting Point Observations

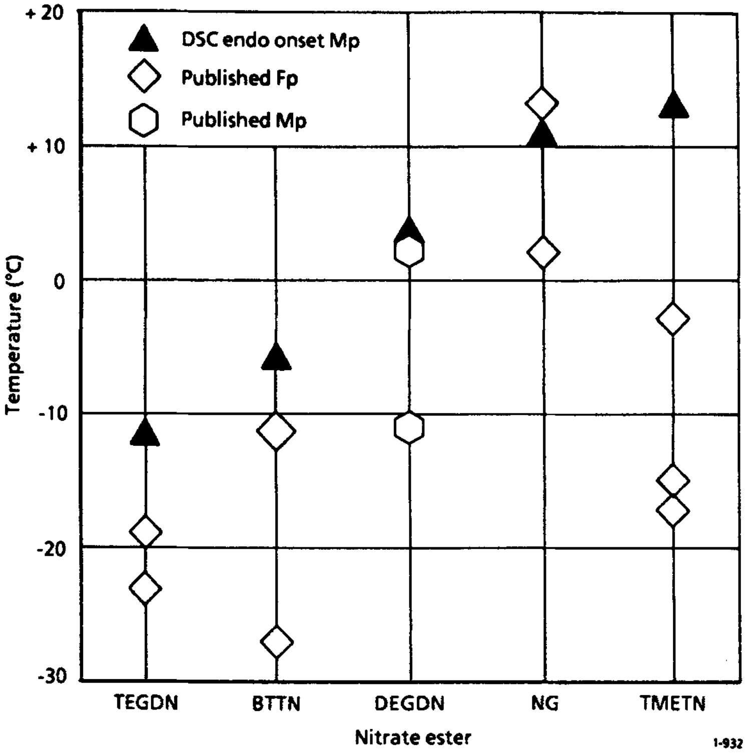

FIGURE 3. DSC Melting Points Do Not Agree Well with Most Published Melting and Freezing Points

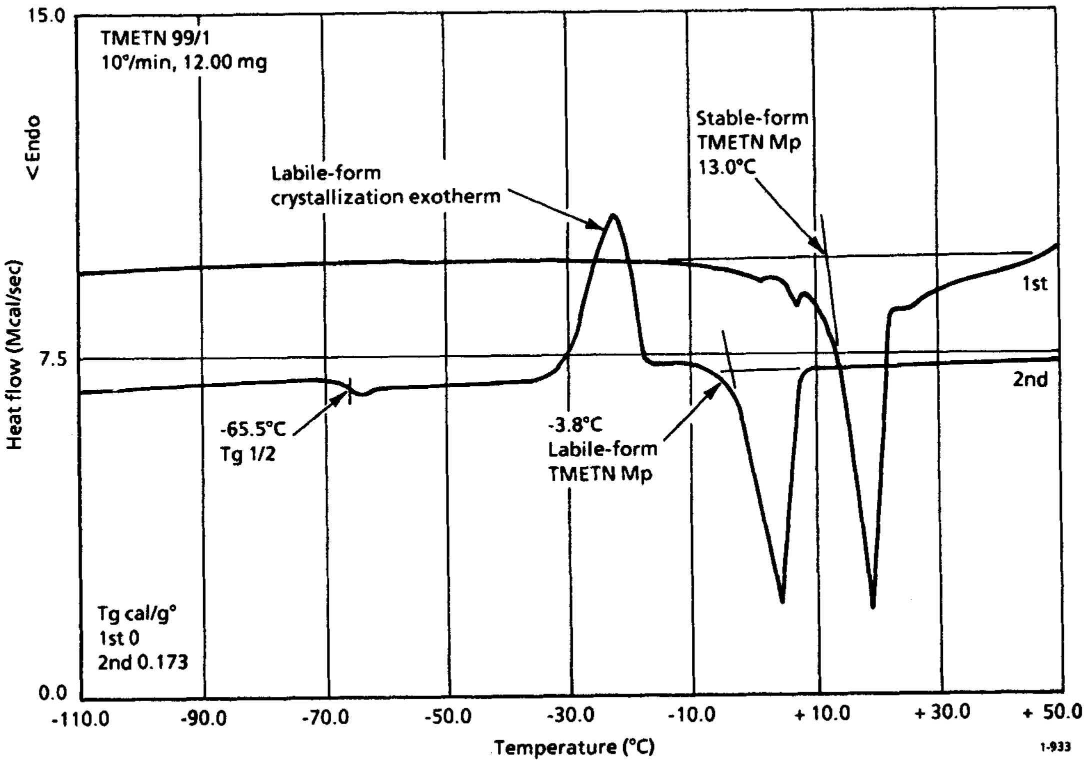

FIGURE 4. First and Second Run DSC Thermograms of Crystallized TMETN

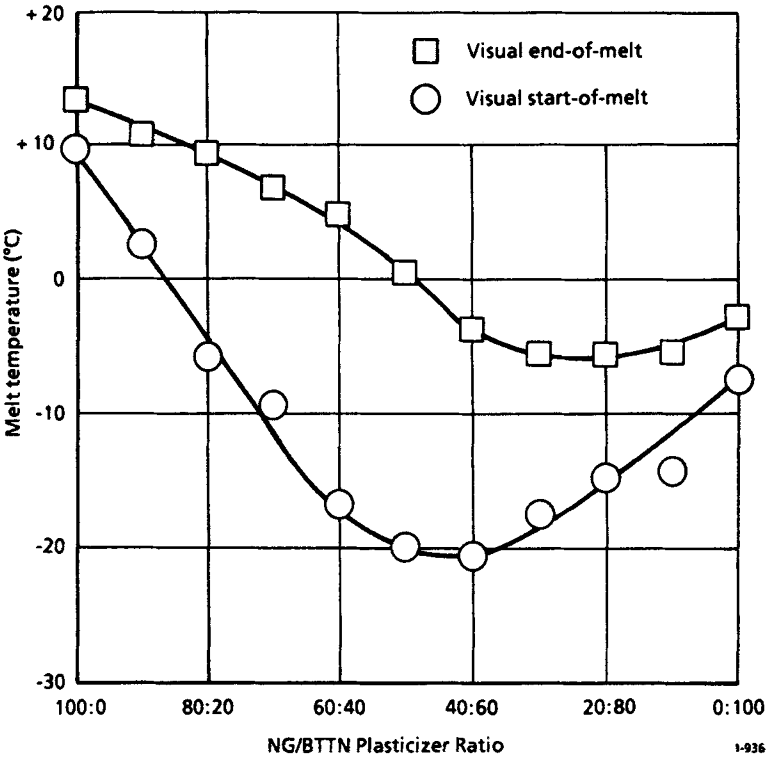

FIGURE 5. Broad Start-to-End-of-Melt Temperature Ranges were Visually Observed for NG/BTTN Mixtures

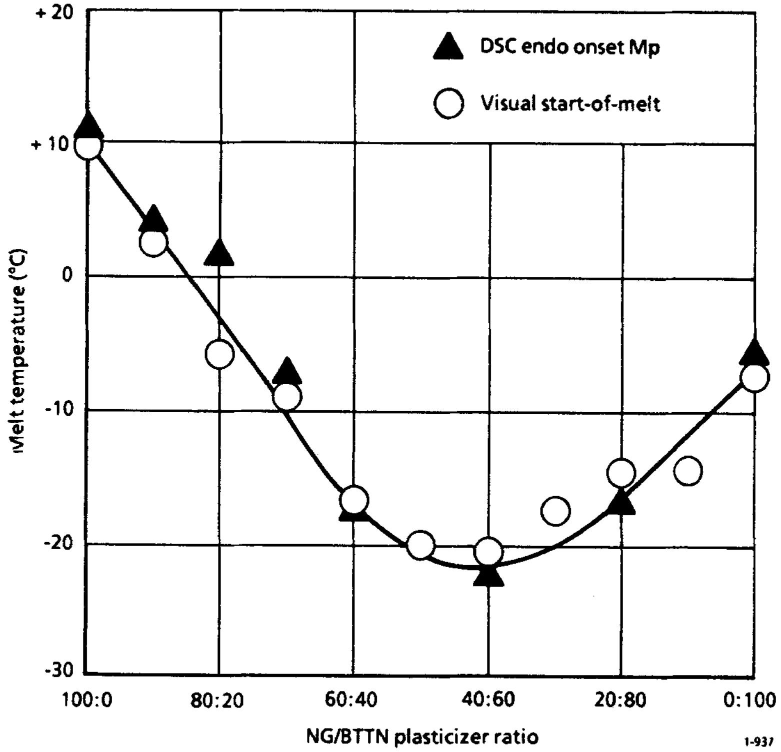

FIGURE 6. DSC Melting Points for NG/BTTN Mixtures Agree with Visual Start-of-Melt Observations

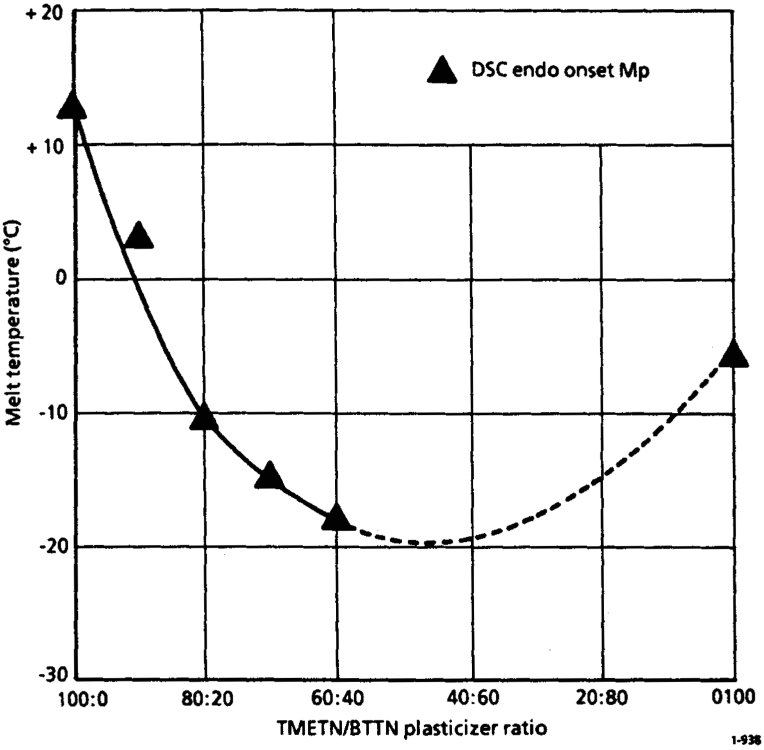

FIGURE 7. DSC Melting Points for TMETN/BTTN Mixtures Approach a Eutectic Similar to the NG/BTTN Mixtures