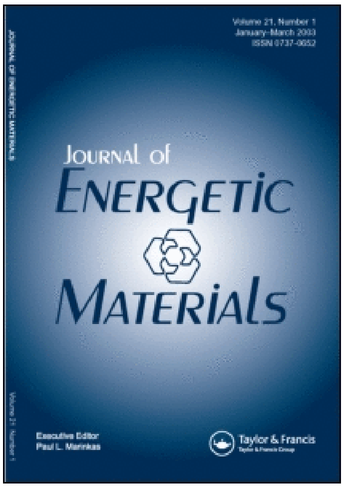

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BINARY PHASE DIAGRAM SERIES: 1,3,3-TRINITROAZETIDINE (TNAZ)/2,4,6-TRINITROTOLUENE (TNT)

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ABSTRACT

The binary phase diagram for the 1,3,3-trinitroazetidine (**TNAZ**)/2,4,6-trinitrotoluene (**TNT**) system has been predicted computationally and determined experimentally. The calculated eutectic temperature/composition is 60.6 °C/35.3 mol percent **TNAZ**. It has been demonstrated that mixtures of **TNAZ** and **TNT** exhibit the thermal characteristics associated with a binary eutectic system affected by component interaction and by apparent polymorphism that is attributed to the **TNAZ** component. It is believed the former causes both the liquidus temperatures and heats of fusion from the initial melting operations to be significantly lower than calculated.

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INTRODUCTION

Archibald and co-workers first prepared 1,3,3-Trinitroazetidine (TNAZ) in 1990[1]. It is a powerful and thermally stable energetic material. Its application to melt cast energetic formulations has been limited by high volatility and a tendency to form low-density castings at atmospheric pressure[2]. Researchers at this laboratory are attempting to ameliorate these unacceptable characteristics by forming binary eutectic compositions with other energetic materials[3, 4, 5, and 6]. To date, binary mixtures of **TNAZ** with pentaerythritol tetranitrate (**PETN**), 2,4,6-trinitrotoluene (**TNT**) and 1,3,5-trinitrobenzene (**TNB**) have been characterized for explosive performance and thermal/shock sensitivity[3, 4, and 5]. It was also demonstrated during a previous investigation[6] that **TNAZ** exists in at least two polymorphic forms, one stable (**TNAZ I**) and one unstable (**TNAZ II**), and that the former is more dense than the latter. Crystal density increases with the spontaneous transition from **TNAZ II** to **I** resulting in a dendritic structure with characteristic macro-shrinkage cracks. These cracks are distributed irregularly throughout a neat **TNAZ** billet from a melt casting operation and are believed to be the primary cause of the measured low bulk density. It has also been reported[7] that **TNT** exists in more than one polymorph and these data have been reproduced during this investigation. The immediate objective of this effort is to experimentally characterize the **TNAZ/TNT** binary eutectic system by using differential scanning calorimetry (DSC) supported by hot stage microscopy (HSM). The overall objective is to generate similar data for a variety of promising **TNAZ**-based binary systems and relate these findings to their shock sensitivities.

EXPERIMENTAL

Phase Diagram Calculation

The eutectic composition and melting temperature for this binary system were calculated by using a computer program in BASIC[8]. The program iteratively solves equation (1) by using component heats of fusion and melting points as input data,

$$R\ln x = \Delta H_{fus}(-1/T + 1/T_o) \qquad (1)$$

where T is the melting point (degree K) of the eutectic composition, T_o, ΔH_{fus} and x are the melting point, heat of fusion and mol fraction of component A or B, respectively, and R is the gas constant (1.987 calories K^{-1} mol^{-1}). Experimental melting points and heats of fusion, determined by DSC heating operations on mixtures of the stable polymorphs of both components, were used for comparison with their corresponding calculated values. Since the BASIC program does not provide a table of liquidus temperatures, they were computationally derived by solving equation (1) for the specific mol fraction values used during this investigation.

Thermal Characterization

a. Differential Scanning Calorimetry (DSC)

TNT, **TNAZ** and selected **TNAZ/TNT** mixtures were thermally characterized by using a TA Instruments Dual Differential Scanning Calorimeter, Model 912, equipped with a 2100 Thermal Analyzer Data System. Standard aluminum sample pans and lids, TA Instruments Part Nos. 072492 and 073191, were used for all melting operations carried out by using the standard Dual Sample DSC (DSDSC) cell. Lids were inverted to minimize free volume over the sample. An upper temperature limit of 105 °C and sample weights not exceeding 4 mg were used throughout this investigation to minimize the chance for leakage from the sample pans.

A minimum of two melting operations was carried out for all mixtures at a heating rate of 1 °C/min. Special DSC experiments were carried out at a heating rate of 5 °C/min with seventeen mixtures to acquire heats of fusion from the initial melting operations. Cooling operations were uncontrolled or accomplished at 5 °C/min by using ice/water as a cooling medium or by quenching the sample pans in liquid nitrogen. Mixtures were prepared by grinding weighed portions of dry energetic materials in an agate mortar with a glass pestle to ensure homogeneity. The DSC was calibrated by using indium metal as a temperature standard. Peak temperatures are reported for all endothermic and/or exothermic processes.

b. Hot Stage Microscopy (HSM)

HSM experiments were carried out by using a Mettler Hot Stage, Model FP 82, equipped with an FP 80 Central Processor. All observations were made with a Leitz Orthoplan Universal Largefield microscope equipped with a polarizing condenser and high-resolution video system, Javelin Smart Camera, Model JE3762DSP, which was operated at shutter speeds of 1/250 or 1/500 s. The video system is also equipped with a FOR-A video timer, Model VTG-55. All photomicrographs were obtained through a Leitz NPL 10X 0.20P lens (150x). Heating and cooling rates were 5 °C/min unless otherwise specified. The cooling rate was not controlled below approximately 45 °C. The temperature at which the last crystal melts is reported as the liquidus temperature. The estimated eutectic melting temperature is differentiated from that of component melting by observing change in the rate of the melting process.

Energetic Components

TNT was recrystallized in a single operation from cyclohexanone and dried under vacuum. **TNAZ** was purified by crash-precipitation from a hot ethanol solution into ice and water.

RESULTS

Thermal Characterization

a. Thermal Properties of TNT and TNAZ

The **TNT** melting point and heat of fusion, 80.6 ± 0.05 °C and 5.101 ± 0.109 kcal/mol, respectively (lit. mp 80.6 to 81.5 °C and ΔH_{fus} 4.585 to 5.403 kcal/mol[7a and b]) were obtained by DSC heating operations at 1 °C/min. The **TNAZ** melting point and heat of fusion are 99.7 ± 0.1 °C and 6.607 ± 0.079 kcal/mol, respectively (lit. mp 101.1 °C/6.405 kcal/mol[6]). **TNT** melting and recrystallization characteristics were also observed by HSM operations. Melting occurred over the temperature range 79.7-81.6 °C with significant premelt darkening. After complete melting and supercooling to less than 37 °C, it recrystallized with an almost formless front and grainy structure (Figure 1). Recrystallization at approximately 75 °C in the presence of seed crystals yielded evidence of polymorphism as described by McCrone[9], where one crystal front grows into the other (Figure 2). Evidence of polymorphism was also observed during DSC operations on quench-recrystallized **TNT**[7c and d]. The **TNT** melting process produced an unresolved endothermic doublet. **TNAZ** was previously shown to exist in at least two polymorphic forms[6].

b. Calculated Phase Diagram

The calculated melting point and mol percent value for the **TNAZ** component in the eutectic composition are 60.6 °C and 35.3, respectively. **TNAZ** mol percent values and associated liquidus temperatures used to construct the phase diagram are shown in Table 1.

c. DSC Characterization of TNAZ/TNT Mixtures

Initial melting operations carried out at a heating rate of 1 °C/min with eleven freshly ground mixtures of **TNAZ** and **TNT** yielded a consistent, endothermic event at an average temperature of 59.7 ± 0.05 °C that is caused by eutectic melting. The endothermic peaks attributed to **TNAZ** melting occurred along a concave-shaped curve positioned below that calculated, while those

Table 1. Mol Percent/Calculated Temperatures Used to Construct the **TNAZ/TNT** Phase Diagram

Mol Percent TNAZ	Temperature (°C)
0	80.6
5.9	77.6
11.6	74.6
22.8	68.4
35.3[1]	60.6
38.5	63.6
49.2	72.2
63.9	81.8
68.7	84.6
78.0	89.6
84.0	92.5
91.4	96.0
95.7	97.8
100.0	99.7

[1] Eutectic composition.

attributed to the melting of the **TNT** component are consistent with the respective calculated liquidus temperatures. Remelting operations on samples obtained by freezing of the initial melts caused the eutectic melting temperature to shift to an average value of 58.5 °C. The experimental **TNT** liquidus temperatures from remelting operations remained consistent with those calculated, whereas those attributed to **TNAZ** again fall below the theoretical liquidus curve. The data from all DSC operations at this heating rate are summarized in Table 2 and displayed graphically with the calculated phase diagram in Figure 3.

Table 2. Endothermic Peak Temperatures for DSC Melting Operations with **TNAZ/TNT** Mixtures at a heating rate of 1 °C/min

Mol Percent **TNAZ**	Temperature (°C)			
	Eutectic			
	Initial	Remelts	**TNAZ**	**TNT**
100			99.7[1,2]	
95.7	59.4	56.0	97.0[1] 97.2[2]	
91.4	59.7	55.9/57.2/58.7	92.8[1] 94.0[2]	
84.0	59.8	58.1	87.2[1] 89.4[2]	
78.0	59.7	58.6	83.5[1] 85.6[2]	
68.7	59.8	58.5	77.2[1] 79.4[2]	
63.9	59.8	58.7	74.7[1] 76.9[2]	
49.2	59.8	59.0	64.6[2]	
22.8	59.9	59.0		68.1[1]/69.2[2]
11.6	59.5	58.2		75.0[1]/75.9[2]
5.9	59.4	57.4		77.5[1,2]
0				80.6[1,2]

1. Initial melting operation.
2. Remelting operation.

DSC melting operations were also carried out on seventeen freshly ground mixtures of **TNAZ** and **TNT** at a heating rate of 5 °C/min. Baseline curvature experienced with the mixtures heated at 1 °C/min prevented the acquisition of usable energy data. The data acquired at this new heating rate are compiled in Table 3.

All of the mixtures are affected by supercooling, with those

Table 3. Endothermic Peak Temperatures for All DSC Melting Operations with **TNAZ/TNT** Mixtures (5 °C/min)

Mol Percent	Temperature (°C)					Hts of Fus. (Kcal/mol)
TNAZ	Init.[1]	Eutectic Rmlt [2]	Reqnd[3]	TNT	TNAZ Init/Rmlt	Calcd/Found[1]
98.3	60.3	54.5			98.9/99.0	6.535/6.394
96.6	60.4	55.8/58.3			98.0/97.9	6.510/6.199
91.4	60.4	57.2/58.7			95.2/95.4	6.433/6.161
84.0	60.7	58.6			91.0/91.2	6.324/6.086
81.6	60.5	58.3			91.6/91.9	6.289/5.078
78.0	60.6	59.0			86.6/87.3	6.236/5.966
68.7	60.6	59.0			83.4/84.0	6.099/5.622
63.9	60.7	59.6			77.2/77.1	6.028/5.453
54.2	60.6	59.3			73.8/71.8	5.885/5.342
50.2	60.9	59.9			67.7	5.826/5.303
44.1	60.6	59.8	60.0		64.4	5.737/5.462
39.3	60.5	59.7			62.0	5.666/5.306
38.5	61.0	60.0				5.654/5.108
34.2	60.6	59.8	59.9	62.1		5.591/5.276
23.5	60.4	59.5		67.8		5.433/5.228
11.6	60.5	58.2	58.1	74.6		5.258/5.031
04.7	60.7	58.3		78.6		5.156/5.051

1. Initial melting operation.
2. Remelting operation.
3. Reground fused mixture from initial melting operation.

closer to the eutectic composition often requiring quenching in liquid nitrogen to initiate recrystallization. The resolidification event for mixtures rich in either component is typically composed of two exothermic peaks, one generally sharp (component recrystallization) and one broad (eutectic recrystallization).

d. HSM Characterization of TNAZ/TNT Mixtures (5 °C/min)

HSM melting operations, carried out on six mixtures, are characterized by two melting processes, eutectic composition followed by that of excess component. All reported temperatures were obtained from operations (remelting) on thin crystalline films that were prepared on a hot plate. The average melting temperature for the eutectic composition, 61.7 ± 0.4 °C, is higher than that obtained from DSC operations due to the difficulty in differentiating between the end of eutectic melting and the start of component melting. All melting temperatures from HSM operations are shown in Table 4.

Table 4. **TNAZ/TNT** Data from All HSM Operations

Mol Percent	Temperature (°C)		
TNAZ	Eutectic	**TNT**	**TNAZ**
81.6	56.4/58.5		93.5
54.2	61.4		77.7
44.1	61.4		67.7
39.3	60.0		64.1
38.5	62.9		
34.2	60.9	63.1	

HSM cooling operations on the molten thin films, as with DSC operations, were hampered by extreme supercooling, especially in proximity to the eutectic composition. For example, a mixture containing 39.3 mol percent **TNAZ** supercooled to below 30 °C, then recrystallized with a continuous, needle-like front. Surface roughening and darkening, which occurred immediately behind the front (Figure 4), is attributed to recrystallization of the eutectic composition. A mixture on the **TNT**-rich side of the eutectic (34.2 mol percent **TNAZ**) supercooled to approximately 14 °C (Figure 5a), then recrystallized with an angular front followed by a time-dependent surface texture change (Figure 5b).

The only recrystallization characterized by a triple event occurred at 43-41 °C with the mixture containing 81.6 mol percent **TNAZ**. The initial liquid to solid transition (Figure 6a) was followed immediately by a solid-solid transition characterized by a distinct transition front and an overall lightening of the thin film (Figure 6b). These two events were then followed by what appeared as a liquid expulsion from the solid matrix and the movement of an apparent crystal front (Figures 6c and d). The first two events are attributed to TNAZ recrystallization followed by a possible polymorphic transition and then by the recrystallization of the eutectic composition.

e. TNAZ/TNT Mixed Fusion

A mixed-fusion slide, prepared by a modification of the method described by McCrone[9], is shown in Figure 7. **TNAZ** was applied to the slide first with coverslip, then **TNT** was melted and allowed to wick under the coverslip until contact was made with the leading edge of the solidified **TNAZ**. The vertical contact line between **TNT** (left) and **TNAZ** (right) extends down the vertical centerline of the photomicrograph. It is sandwiched between a wide zone of mixing characterized by multi-colored plates oriented in a horizontal direction on the **TNT**-rich side and an area of fine particles on the side rich in **TNAZ**. Characteristic **TNT** and **TNAZ** thin film structures are seen on the far left and far right, respectively. Eutectic melting occurred rapidly at the point of contact over the range 59.4-61.0 °C (Figure 8) and continued slowly until **TNT** and **TNAZ** had completely melted at 80.7 and 99.8 °C, respectively. Upon cooling, **TNAZ II** recrystallized at 52.7 °C with a continuous, formless front (Figure 9a), then spontaneously converted to **TNAZ I** (Figure 9b) and continued to grow rapidly into the zone of mixing as large, well-defined platelet-like crystals (Figure 9c). The growth rate of these platelets slowed rapidly in the area of the eutectic mixture. **TNT** began to recrystallize at 32.9 °C, moved rapidly through the **TNT** melt with a continuous, formless front (Figure 10a), then across the eutectic area and the large **TNAZ** platelets (Figure 10 b) and finally across the entire visible **TNAZ** section of the slide (Figure 10c).

DISCUSSION

Evidence believed to be associated with polymorphism was observed by DSC operations on neat, quench-cooled **TNT**. The polymorph melted approximately 1 °C lower than the stable polymorph obtained by solvent-recrystallization. Since the two endotherms associated with melting were not completely resolved, individual heats of fusion were not afforded. The experimental melting point and heat of fusion used for all calculations during this investigation were obtained by DSC operations on solvent-recrystallized **TNT**. Other evidence, also reported to be associated with polymorphism[9], was observed during HSM operations. **TNT**, when recrystallized from the melt at approximately 75 °C in the presence of seed crystals, produced plate-like crystals that grew into and through one another. As previously described[6] and shown in Figure 9b, polymorphism was also observed during HSM recrystallization operations with neat **TNAZ**.

TNT liquidus temperatures from DSC heating operations on freshly ground mixtures were consistent with theory. Similarly, the average melting temperature (59.7 ± 0.05 °C) of the eutectic composition from initial DSC heating operations agreed closely with the calculated value (60.5 °C). These two findings suggest that the stable polymorph of **TNAZ**, (I), is participating in the initial eutectic melting process.

The experimental **TNAZ** liquidus temperatures, however, form a continuous, concave-shaped curve that is positioned below the calculated curve. In addition, the heats of fusion associated with these **TNAZ**-rich mixtures were all less than the theoretical values, with the largest deviations (approximately 10 percent) occurring between 68.7 and 38.5 mol percent **TNAZ**. The coefficient of determination (R^2) for a 2nd order polynomial trendline through these data points that is forced through the highest eutectic melting temperature (59.9 °C) positioned at the calculated eutectic composition (35.1 mol percent **TNAZ**) was 0.9993. These data suggest a component interaction such as solid solution formation.

Remelting operations did not appreciably affect the **TNT** liquidus temperatures; however, those attributed to eutectic melting were shifted to a lower temperature range (57.2-59.0 °C) with an average value of 58.5 ± 0.02 °C. More than one endotherm that appeared to be associated with eutectic melting occurred above 90 mol percent **TNAZ**. **TNAZ** remelting temperatures were shifted to slightly higher values relative to those from the initial melting operations. A linear trendline through these temperatures with a coefficient of determination of 0.997 intersects the extension of the calculated **TNT** liquidus curve at 58.6 °C and 38.2 mol percent **TNAZ**. This intersection temperature is consistent with the experimental eutectic remelting temperature (59.0 °C) for compositions between 49.2 and 22.8 mol percent **TNAZ**. While it is conceivable this eutectic melting temperature shift may be associated with crystal intimacy resulting from the initial fusion process, it is believed the data more strongly suggest it is caused by **TNAZ** polymorphism. This **TNAZ** polymorph is a product of the recrystallization process that occurs after the initial melting operation. It was demonstrated that this temperature shift does not result simply from operating on a fused sample versus freshly ground crystals (see Table 3).

CONCLUSIONS

The binary phase diagram for the **TNAZ/TNT** system has been predicted computationally by using the measured heats of fusion and melting points of the components. It has been demonstrated during this investigation that mixtures of **TNAZ** and **TNT** exhibit the thermal characteristics associated with a binary eutectic system affected by a component interaction and by polymorphism that is believed to be attributed solely to the **TNAZ** component. The deviation of the **TNAZ** liquidus temperatures obtained from initial melting operations from those calculated is believed to result from a component interaction, e.g., solid solution formation. The shift of the **TNAZ** liquidus temperatures and those associated with eutectic melting that are observed during remelting operations are attributed to **TNAZ** polymorphism. It is believed this polymorph is produced from the recrystallization process following the initial melting operations. Both components, as well, exhibit properties in the neat state that have been reported to be characteristics associated with polymorphism. When a molten casting of neat **TNT** is allowed to supercool extensively, large orthorhombic crystals will form along with the desired monoclinic crystals. The former generally contains intergranular voids that may lead to increased shock sensitivity. This potential problem is avoided by the incorporation of monoclinic seed crystals during the cooling process.

An unacceptable low density, usually around 90 percent of theoretical maximum (crystal) density, characterizes a billet of neat **TNAZ** obtained from a melt casting operation. The increased void volume in the billet is attributed to the formation of its lower density, unstable polymorph (**TNAZ** II) during the recrystallization process. It has been previously shown that **TNAZ II** spontaneously transitions to the more dense, stable polymorph (**TNAZ** I) with an accompanying irregular distribution of macro-shrinkage cracks.

The low billet density problem was overcome by using a eutectic mixture of **TNAZ/TNT** where a density of 96-97 percent of TMD was obtained, an acceptable billet density range for melt cast, **TNT**-rich systems. The influence of the **TNAZ** polymorphic transition is not significant relative to final billet density. This binary eutectic system is one of several containing **TNAZ** that have been and are being investigated in a effort to find a usable binder for melt castable formulation application.

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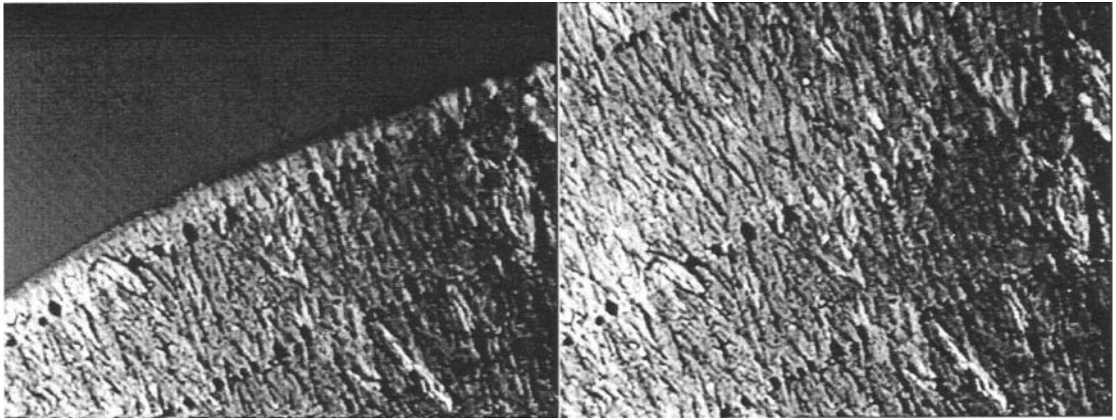


FIGURE 1.

Thin film of **TNT** crystallizing at 36.7 °C.

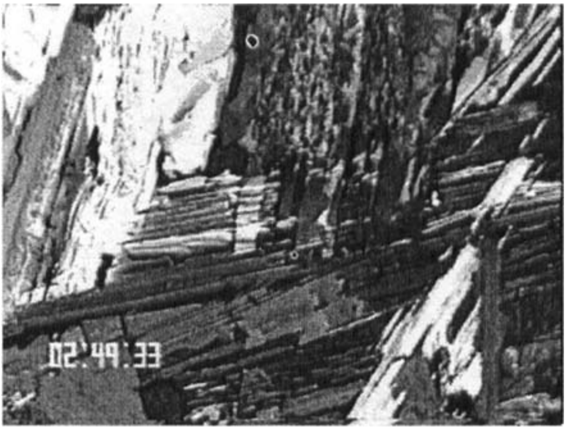


FIGURE 2.

Thin crystalline film of **TNT** recrystallized at 75 °C in the presence of seed crystals.

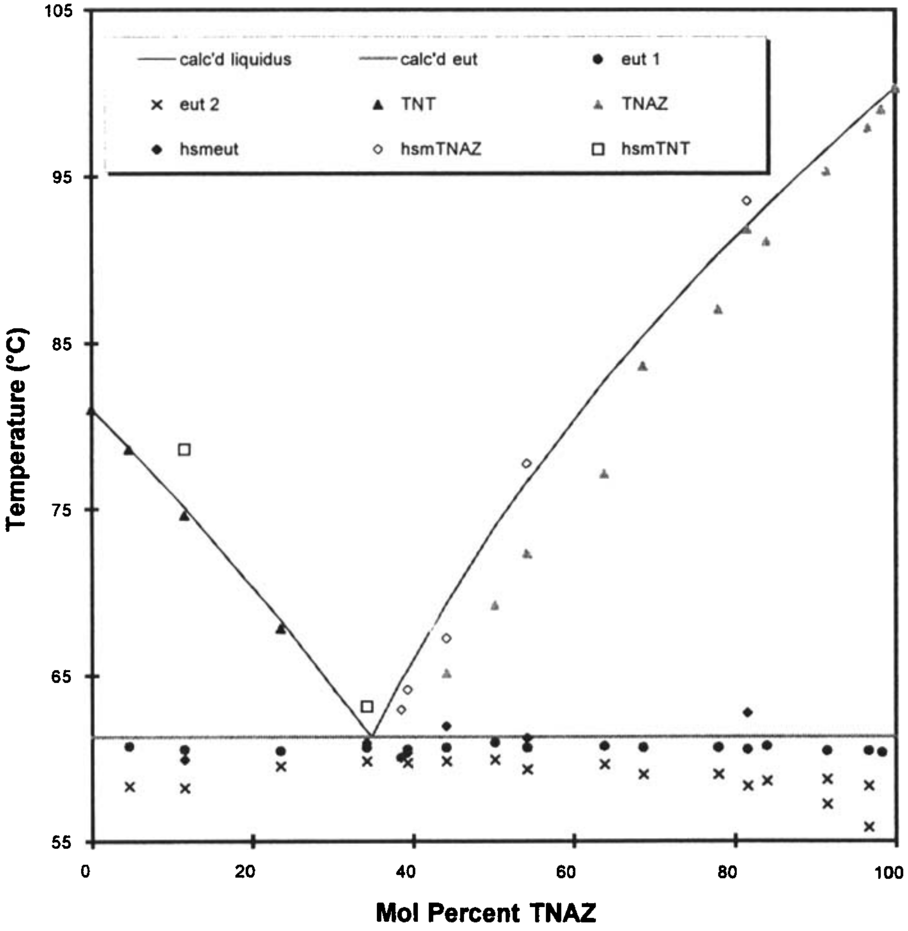


FIGURE 3.

Calculated phase diagram for the **TNAZ/TNT** system with supporting experimental data.

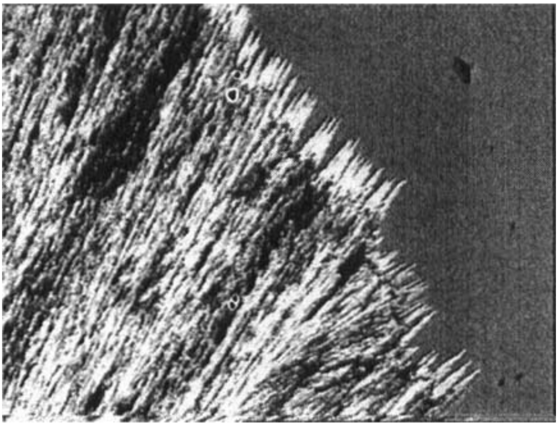
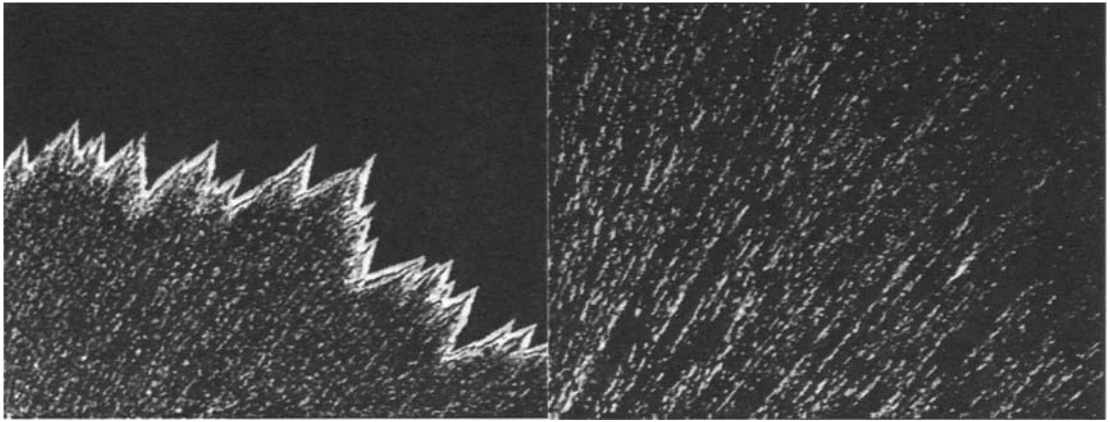


FIGURE 4.

Mixture containing 39.3 mol percent **TNAZ** recrystallizing at 29 °C as an apparent single-event process with a needle-like front.



a.

b.

FIGURE 5.

Mixture containing 34.2 mol percent **TNAZ**, a) recrystallizing at approximately 14 °C and b) exhibiting a time-related surface texture change/darkening.

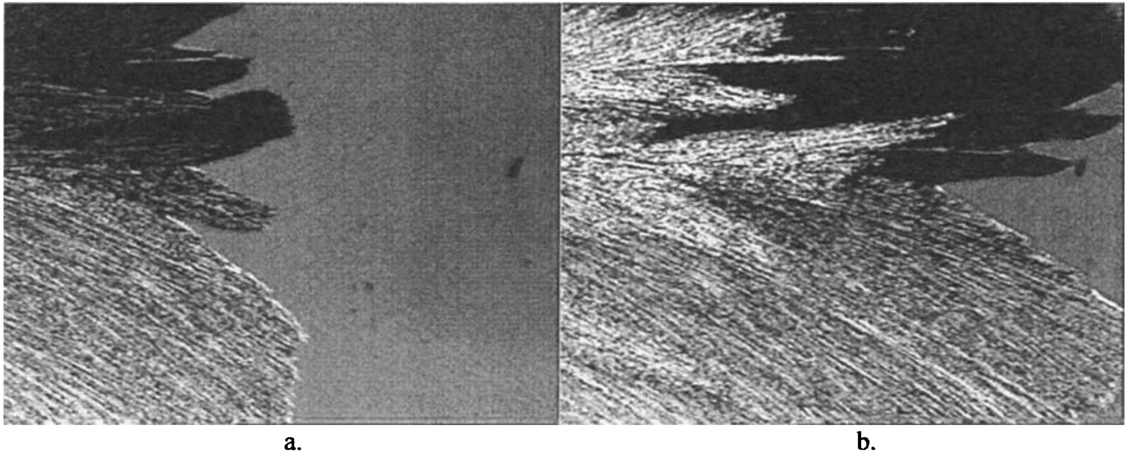


FIGURE 6.

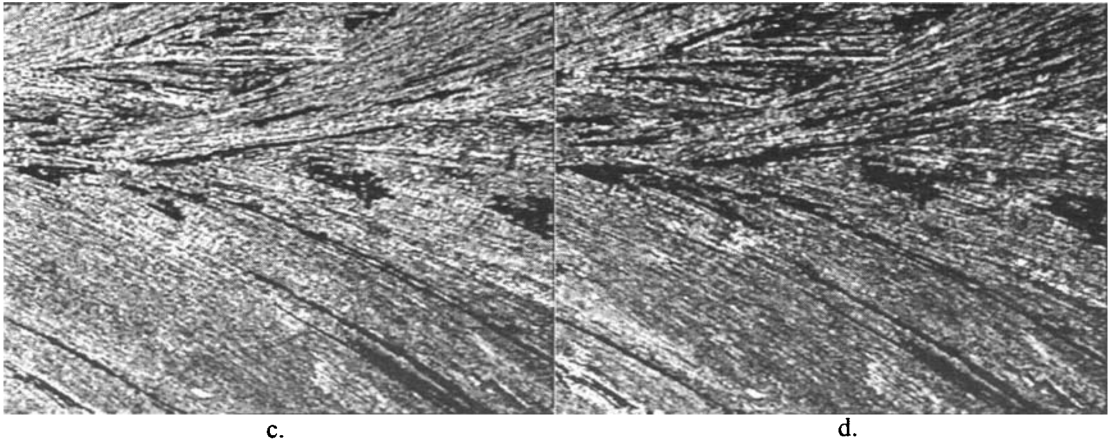


FIGURE 6.

Recrystallization of a mixture containing 81.6 mol percent **TNAZ**, a) initial unstable **TNAZ** polymorph, b) transition to stable **TNAZ** polymorph, c) recrystallization of eutectic and d) final thin crystalline film.

FIGURE 7.

Mixed fusion type thin crystalline film of **TNT** (left) and **TNAZ** (right).

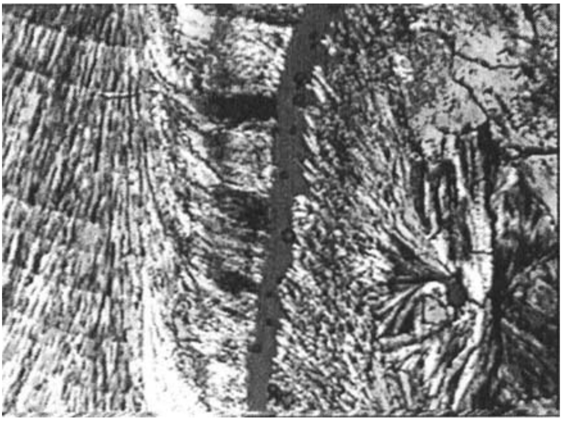


FIGURE 8.

TNAZ/TNT mixed fusion thin crystalline film showing eutectic melting in the temperature 59.4-61.6 °C.

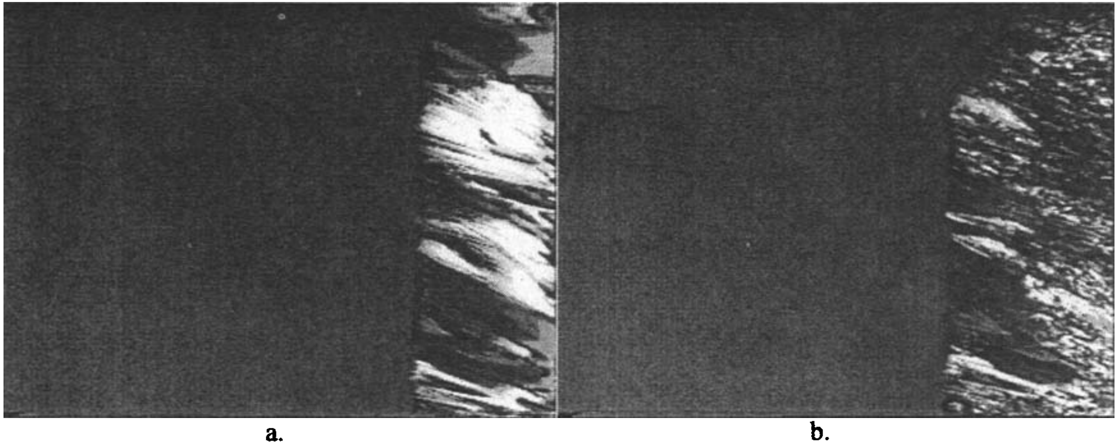
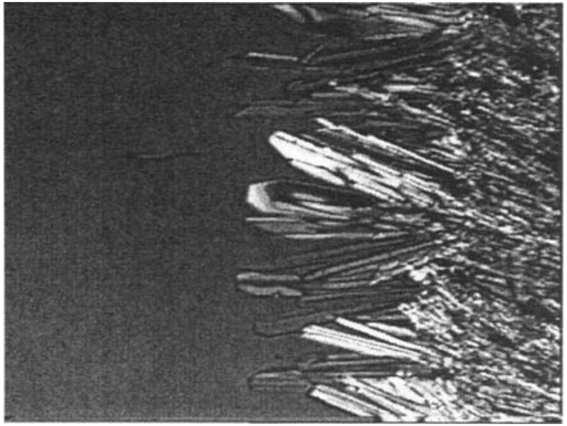


FIGURE 9.



c.

FIGURE 9.

Mixed fusion thin crystalline film: a) **TNAZ** polymorph (believed to be **TNAZ II**) recrystallizing at 52 °C, b) **TNAZ II** spontaneously transitioning to another polymorph (believed to be **TNAZ I**) and c) **TNAZ** crystals growing into the zone of mixing.

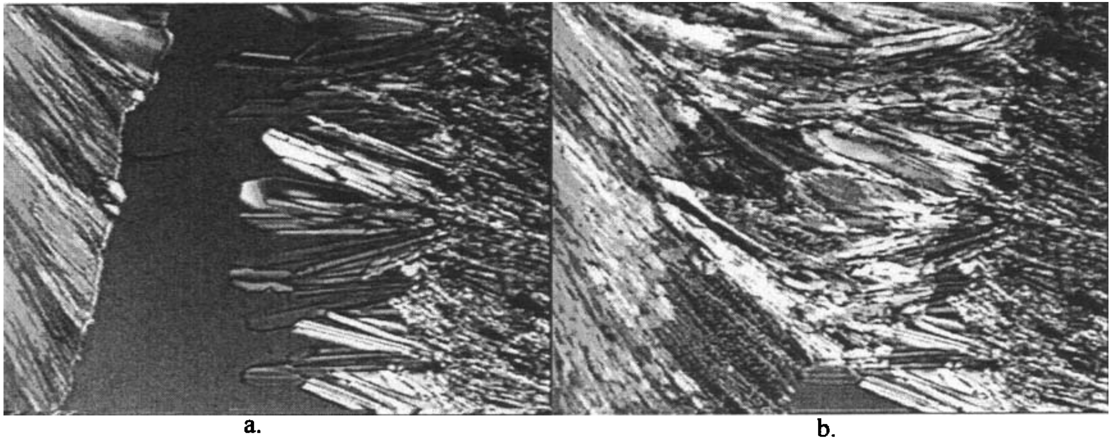


FIGURE 10.

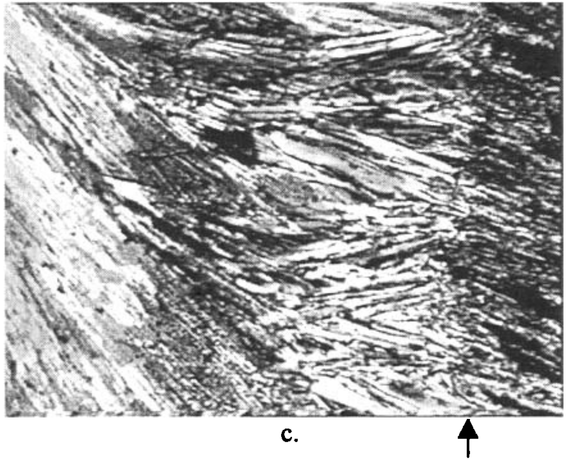


FIGURE 10.

Mixed fusion thin crystalline film: a) **TNT** recrystallizing at 32.9 °C with a formless front, b) front crossing over **TNAZ** crystals and c) front beginning to cross over main **TNAZ** thin film (arrow).