

MELTING BEHAVIOR AND PHASE DIAGRAM OF ISOMERIC DIISOCYANATES

R. G. Ferrillo and A. H. Granzow

AMERICAN CYANAMID COMPANY, CHEMICAL RESEARCH DIVISION, 1937 WEST MAIN STREET, P.O. BOX 60, STAMFORD, CT 06904-0060, USA

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Differential scanning calorimetry (DSC), thermogravimetry (TG), thermomicroscopy, and FTIR/thermomicroscopy have been used to study the thermal properties of two novel diisocyanates, 1,4-bis(1-isocyanato-1-methylethyl)benzene (P) and its isomer, 1,3-bis(1-isocyanato-1-methylethyl)benzene (M). Properties measured include the heat of fusion, melting point, volatility profile, and phase behavior. The variation of the melt behavior of (P)/(M) mixtures with composition has also been studied.

Diisocyanates are widely used in the production of polyurethane elastomers, coatings, and foams. Several thermal studies of the urethane reaction have been reported [1-3]. However, the thermal properties of the diisocyanates themselves are scarcely documented.

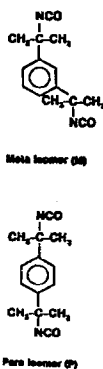


Fig. 1 Structure of (M) and (P)

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In this report, we describe the phase behavior of two novel isomeric diisocyanates, 1,4-bis(1-isocyanato-1-methylethyl)benzene (P) and 1,3-bis(1-isocyanato-1-methylethyl)benzene (M); their structures are depicted in Fig. 1. The chemical structures of these two compounds are somewhat unusual: Although they contain the aromatic ring system, they exhibit the desirable properties of aliphatic diisocyanates [4]. This is due to the effect of the isopropylidene groups adjacent to the aromatic ring which effectively isolate the isocyanate groups from the aromatic ring system. Basic physical properties of both (P) and (M) have been reported [5]. The adduct formation of (M) with trimethylol propane has been investigated by size exclusion chromatography [6].

Experimental

Materials

The following materials were used: 1,4-bis(1-isocyanato-1-methylethyl)benzene (P), an American Cyanamid Company research sample, and 1,3-bis(1-isocyanato-1-methylethyl)benzene (M), a product of American Cyanamid Company. These two materials are registered under the Trademarks TMXDI[®] (PARA) and TMXDI[®] (META) respectively.

Procedures

Differential Scanning Calorimetry (DSC)

A DuPont 990 Thermal Analyzer equipped with a standard DSC cell, a Mettler TA-2000B DSC and a Mettler TA 3300 DSC were used in this study. The temperature and heat flow calibrations were carried out using high purity indium, according to each manufacturer's specifications. Samples were hermetically sealed in a dry nitrogen-purged glove box. As recommended by Mettler Instrument Corporation, a dry nitrogen purge of ~25 mL/min was maintained in the Mettler TA-2000B system during heating and cooling; no purge gas was used in the Mettler TA-3300 system. A dry nitrogen flow rate of ~25 mL/min purged the Dupont 990 system.

Thermogravimetry (TG)

The temperature axis of the Perkin-Elmer TGS-2 thermogravimetry instrument was calibrated with Curie point standards according to the

manufacturer's specifications; the weight axis was calibrated with standard Class M weight obtained from the National Bureau of Standards. Uncovered samples were purged at ~25 mL/min in either dry nitrogen or dry tank air.

Thermomicroscopy

Mettler FP5/52 instrumentation was used for thermomicroscopy experiments. The temperature scale was calibrated with standard materials supplied either by Mettler Instrument Corporation or Arthur H. Thomas, Inc. Samples were prepared under ambient conditions. A cover glass, placed over the sample prior to scanning, minimized contact with air.

FTIR/Thermomicroscopy

The tandem FTIR/thermomicroscopy instrumentation consisted of a Digilab FTS-15E with its microsampling accessory. This accessory was modified to accept the Mettler FP-5 micro heating stage. All glass windows of the FP-5 and the cooling fan were removed. Temperature calibration with melting point standards was necessary.

Results and discussion

Volatility

The TG thermal curve of (M) in nitrogen is shown in Fig. 2. Based on the curve shape, the volatilization, which begins at about 50°C, occurs in two stages; no residue is observed.

The corresponding TG thermal curve of (P) is shown in Fig. 3. Under the TG conditions of rapid gas stream, volatilization begins at about 100°C. Again, two consecutive volatilization processes are apparent and a residue of about 6% is observed. These TG profiles suggest that both (M) and (P) decompose in the condensed phase prior to volatilization. Volatilization profiles are not affected by a change to air as the purge gas, indicating that the condensed phase decomposition is due to pyrolysis rather than thermooxidation.

Phase behavior

On cooling the liquid (M) at 10 deg/min, only a glass transition is observed on the DSC thermal curve. However, on heating the same sample

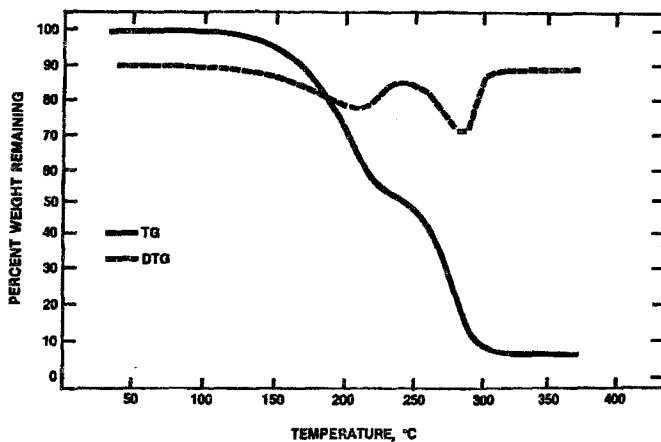


Fig. 2 TG curve of (M) in nitrogen. Heating rate: 10 deg / min

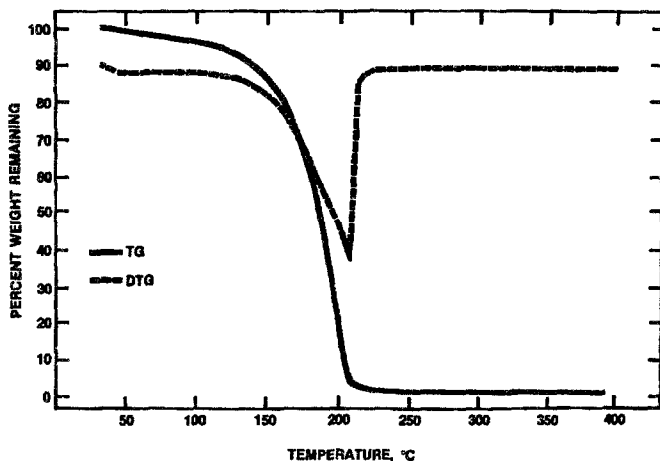


Fig.3 TG curve of (P) in nitrogen. Heating rate: 10 deg /min

from -140 to 30°C at 10 deg/min, three different thermal events are seen, namely a glass transition, an exotherm thought to represent crystallization of the glass, and an endotherm thought to represent melting - Fig. 4. (Note that temperature control was maintained during both heating and cooling.) The thermal event superimposed on the glass transition is too small to be

evaluated precisely; the three thermal processes were quantitated by standard DSC techniques and are shown in Table 1.

Table 1 DSC (M)

Glass transition	-85°C
Heat of crystallization	$-(60 \pm 3) \text{ J/g}$
Heat of melting	$+(74 \pm 4) \text{ J/g}$

The thermal event superimposed on the glass transition is assumed to represent a stress relaxation phenomenon: Cooling the sample below its glass transition yields a rigid structure with restricted bond rotation; heating the sample above its glass transition greatly enhances rotation. The

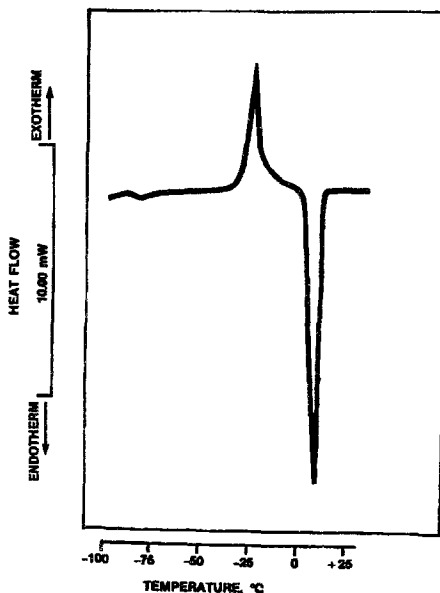


Fig. 4 DSC curve of (M) in nitrogen. Heating rate: 5 deg/ min

variability in enthalpy values indicates variability in the completeness of crystallization between various DSC runs: In each case a glass is obtained initially. Crystallization of this glass, i.e. crystal nucleation and growth, is dependent on kinetic factors. Consequently, degree of crystallization is not reproducible between runs. The glass transition, measured as the mid

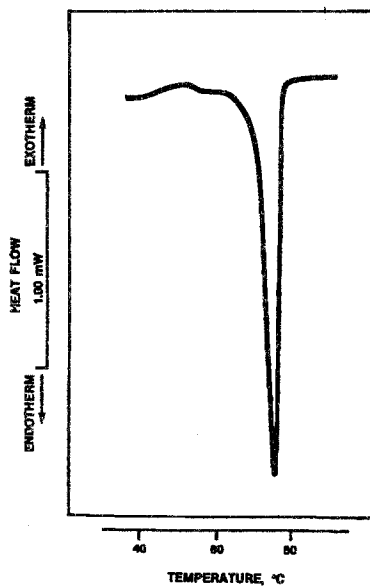


Fig. 5 DSC curve of (P) in nitrogen. Heating rate :10 deg /min

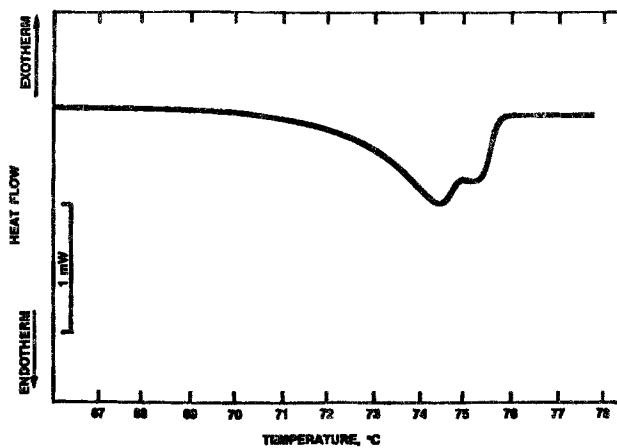


Fig. 6 DSC curve of (P) in nitrogen. Heating rate: 0.5 deg /min

point of the specific heat change, shows no variability when measured on both the heating and cooling curves.

When heated at 10 deg/min, the thermal curve of a sample of the para isomer, on the other hand, indicated melting as the only thermal event - Fig. 5. A heat of fusion of (38.3 ± 2.0) J/g was obtained upon integration of the melt endotherm.

However, when heated at a slow scan rate, i.e. 0.5 deg/min, two overlap-

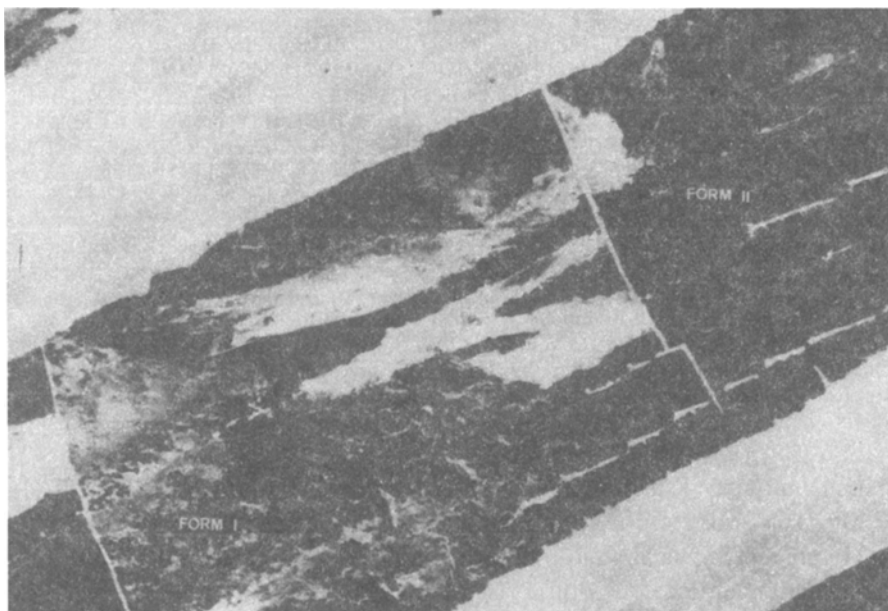


Fig. 7 Photomicrograph of polymorphic forms of (P)

ping endotherms are observed for (P), as shown in Fig. 6. Attempts to recrystallize the compound in situ were not successful. Though polymorphism was suspected, DSC did not prove conclusively that the compound is indeed polymorphic. Thermomicroscopy was selected as the appropriate technique to confirm the DSC observations.

By using the hot stage microscope, two crystal forms were indeed observed. Figure 7 illustrates the transformation of the high temperature phase to the ambient phase. The ambient phase is conventionally designated as

Form I, while the high temperature stable phase is designated as Form II (7). In Fig. 7, Form II appears as large blades which are highly oriented and Form I as the fine grained phase which is less oriented. In general, crystal habit is governed by both nucleation and condition or rate of growth. Based on the structure of the isocyanate, rotation around the C-C bonds, which in-

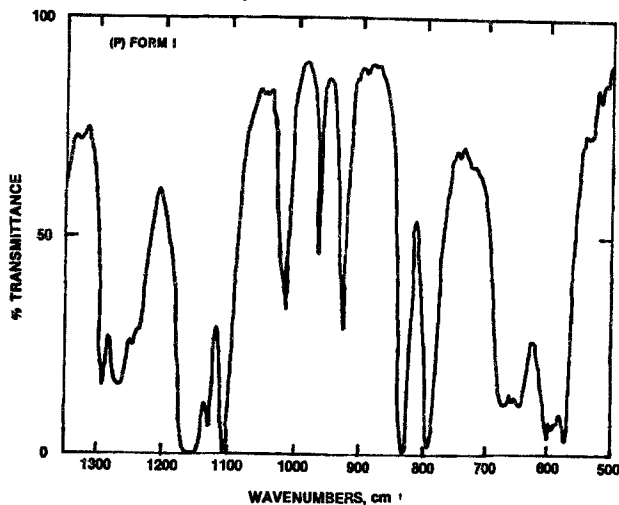


Fig. 8 FTIR spectra of polymorphic form I of (P)

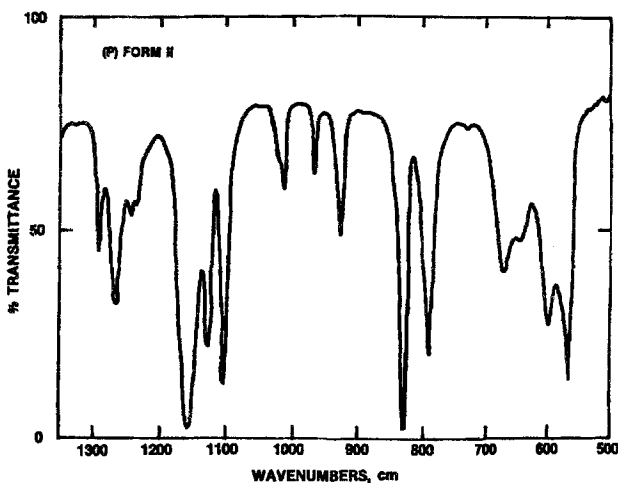


Fig. 8a FTIR spectra of polymorphic form II of (P)

volves low energy, is thought to be responsible for polymorphism of the para isomer.

By adapting a Mettler hot stage to the FTIR, we were able to obtain the IR spectrum of both polymeric forms. The spectrum of the ambient stable phase can be easily obtained. However, complete conversion to the high temperature form, Form II, can only be accomplished at elevated temperature. Therefore, the hot stage adaptation is required to accord the spectrum in the temperature range where the phase is thermodynamically stable. As noted earlier, the ambient stable phase, Form I, is fine grained. During transformation to Form II, each grain is transformed individually. Consequently, orientation effects should not be an important factor in the interpretation of the infrared spectra. By comparing the spectra of the two polymorphic forms of (P) with the spectrum of a randomly oriented sample of the para isomer, orientation effects were found to be minimal. In Fig. 8, absorptions at 1160 and 1265 $1/\text{cm}$ illustrate differences between the two forms. The bands at 1160 and 1265 $1/\text{cm}$ are weaker and stronger respectively than in the random material due to the pendant groups. Bands in the region of 800-1100 $1/\text{cm}$ probably illustrate three changes in dipole moment. Again the subtlety of these changes emphasizes the low energy rotational changes between these polymorphic forms, suggesting group disorder changes in rotational frequency. The melting enthalpy value obtained for the para isomer suggests that there is no large change in the lattice as a result of the transformation, further supporting the infrared observations.

Composition Diagram of Isomer Mixtures

The melt endotherms from DSC thermal curves observed for a series of mixtures of (M) and (P) were integrated and the resulting heats plotted vs mixture composition. Figure 9, the resulting binary composition diagram, shows that the isomeric isocyanates appear to form a simple eutectic. Composition of the eutectic is one part para to two parts meta. However, the large uncertainty in the crystallization enthalpy of the meta isomer impacts on the enthalpy vs composition diagrams. Figure 10 shows the relationship between temperature and composition. The isomers are mutually soluble, i.e. a lowering of the melting point of each pure isomer is observed.

The lowest melting mixture is the the eutectic. However, thermomicroscopy failed to establish the nature of the binary composition diagram: The meta isomer (M), a liquid under ambient conditions, supercools to a glassy state, as noted above. The thermoelectric cold stage used for this study

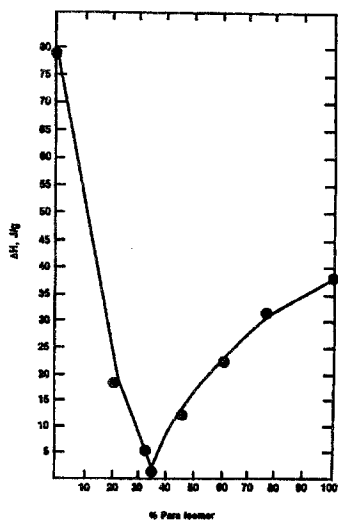


Fig. 9 Binary composition diagram of mixture of (M) and (P)

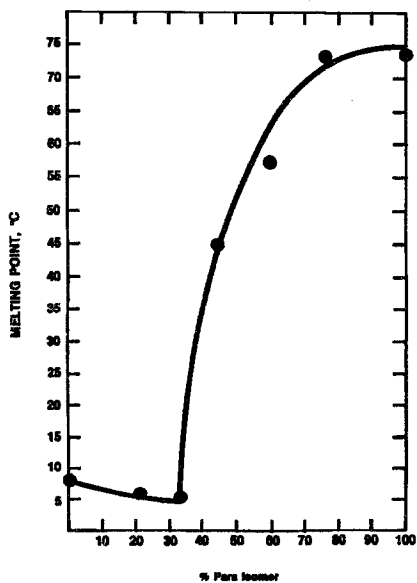


Fig. 10 Temperature vs. composition diagram of mixtures of (M) and (P)

would not lower the temperature below -20°C . Under these conditions it was not possible to induce crystallization.

Conclusions

Both meta and para isomers of these novel diisocyanates decompose prior to volatilization under TG conditions.

The DSC thermal curve of the meta isomer shows four thermal events upon heating: Glass transition with subsequent stress relaxation, partial crystallization, and melting. The DSC trace of the para isomer shows the melting points of two polymorphs which are characterized by crystal structure and IR spectra.

The two isomeric diisocyanates are soluble in the melt in all proportions. The phase diagram shows a eutectic corresponding to the composition two meta isomer per para isomer.

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Zusammenfassung - Mittels DSC, TG, Thermomikroskopie und FTIR/Thermomikroskopie wurden die thermischen Eigenschaften von 1,4-Bis(1-isocyanato-1-methylethyl)benzol (P) und seines isomers 1,3-Bis(1-isocyanato-1-methylethyl)benzol (M), zweier neuartiger Diisocyanat, untersucht. Zu den ermittelten Eigenschaften gehören Schmelzwärme, Schmelzpunkt, Verdampfungsprofil und Phasenverhalten. Die Veränderung des Schmelzverhaltens von (P)/(M)-Gemischen in Abhängigkeit von der Zusammensetzung wurde ebenfalls untersucht.