

Aromatic Polyamides. VI. Thermal Behavior of Model Diamides

Many liquids can be solidified in the glassy state if they are cooled more rapidly than the time required for crystal nuclei formation. This is easy to do with polymers which, because of their longer chain structures and chain entanglements, cannot fit into the crystal lattice upon rapid cooling. However, low-molecular-weight materials are difficult to obtain in the glassy form. Although glass transition is exhibited by many low-molecular-weight compounds,^{1,2} it is by no means universal as it is for polymeric materials. During the course of characterizing some aromatic diamides (mol wt 315–385), we observed that these compounds exhibit very large super coolings and can be quenched to the glassy state just like poly(ethylene terephthalate).

In this note we describe the phenomenon of *glass transition*, *cold crystallization*, and *melting* of some aromatic diamides. Structural effects on these transitions and *thermal stability* are also considered.

EXPERIMENTAL

Synthesis: The synthesis of the diamides has been described elsewhere.³

Thermal characterization: Thermogravimetric analysis (TGA) was performed on all the compounds using a DuPont 990 thermal analyzer with a 951 TGA module. The experiments were carried out in argon atmosphere with about 30-mg sample size and at a heating rate of 10°C/min.

Thermal transitions were studied by differential scanning calorimetry (DSC) using a DuPont 990 analyzer. The studies were made with a 10-mg sample and at a heating rate of 10°C/min in argon atmosphere. Heat of fusion measurements were carried out in a Perkin-Elmer DSC-2 unit with an interfaced programmable calculator. The measurements were made in argon atmosphere and at a 10°C/min heating rate with a 2.5–3.5-mg sample size.

X-ray Diffraction: The diamides were analyzed for the % crystallinity by X-ray diffraction technique. The diffraction patterns were obtained on a Norelco diffraction system configured as follows: 40 kV, 30 mA, rate meter recording, 2° 2 θ /min., time constant of 2 sc, crystal monochromated CuK α radiation, pulse height analysis, and ambient room conditions.

RESULTS AND DISCUSSION

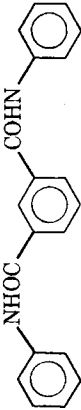
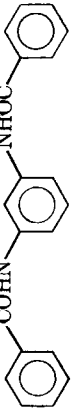
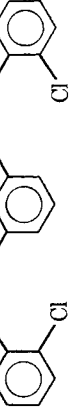
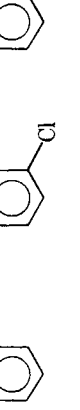
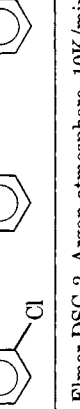
Melting Behavior

The thermal transitions of the diamides are described in Table I. The diamides I, II, and III (dried at 125°C for 6 h) appeared to be fully crystalline by X-ray. From the melting point (T_m) and enthalpy of fusion (ΔH_m) data, the entropy of fusion (ΔS_m) values were calculated for these compounds using the relationship: $T_m = \Delta H_m / \Delta S_m$.

Comparing the isomeric diamides I and II, it is clear that the higher melting point of I is due to its higher heat of fusion. The differences in ΔH_m must arise due to variations in the molecular interactions; the latter are comprised of hydrogen bonding in addition to van der Waal's forces in these materials. X-ray diffraction experiments show that the two compounds have different crystal structures (Fig. 1). Although the detailed crystallographic studies of these diamides have not been carried out, it is not unreasonable to assume that a higher ΔH_m involves a closure chain packing which may enhance the hydrogen bonding as well. Surprisingly the entropy of fusion of compound I is higher than that of II. As a result of the conjugation of the central benzene ring with two *m*-carbonyl groups, one would have expected diamide I to be more rigid molecule and thus show lower ΔS_m . The lower entropy of fusion of diamide II compared to I may somehow be related to its stronger retention of hydrogen bonding in the melt. The melting temperatures of compounds I, II, and III were found to be thermal-history-independent.

The addition of two chlorine substituents in diamide I structure causes a drastic decrease in the T_m as a result of lower ΔH_m as well as higher ΔS_m . Diamides IV and V were found to have appreciable amorphous fractions even after extended annealing. The semicrystalline nature of these two compounds is not understood, and as a result no particular attention has been given to interpret their transitions.

TABLE I
Thermal Transitions of Aromatic Diamides^a

No.	Diamide Structure	Mol wt	Initial heat up			Glass transition (T_g) (°C)	Reheat ^{b,c}	
			Melting temp (T_m) (°C)	Enthalpy of fusion (ΔH_m) (kcal/mol)	Entropy of fusion (ΔS_m) (cal/mol·K)		Crystallization temp [$T_c(t_s)$] (°C)	Melting (T_m) (°C)
I		316.0	290	14.72	26.15	94 (?)	158	291
II		316.0	247	12.11	23.29	65	115 + 132	247
III		385.0	198	12.08	26.65	33	74 + 128	198
IV		350.5	180 ^d					
V		350.5	165 ^d					

^a Perkin-Elmer DSC-2, Argon atmosphere, 10K/min. heating rate, 3.0 ± 0.5mg sample in crimped Al pans. Tektronix-31 interfaced calculator used to evaluate the ΔH values.

^b Upon quenching the sample from above the melt, in liquid nitrogen.

^c Underlines indicate the major transitions.

^d Broad melting.

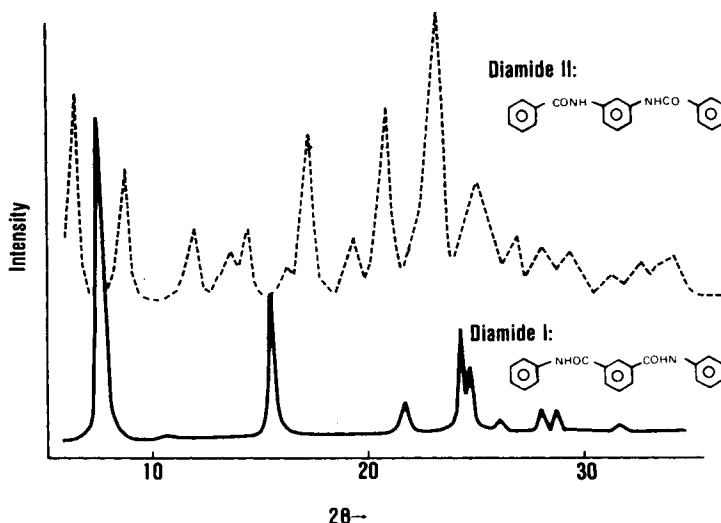


Fig. 1. X-ray diffractometer scans for two isomeric diamides.

Glassy Behavior

During the recrystallization step of the preparation of these materials, it was observed that only the diamide I had a shiny crystalline form; the others precipitated out as powders. The latter, we believe, may have developed crystallinity during the drying procedure. None of the diamides exhibited any transition other than melting during the initial heatup. However, when quenched from above the melt and reheated, most of the compounds showed glass transition (T_g) and crystallization upon heating [$T_{c(h)}$] followed by melting (Fig. 2).

No successful attempts could be made to obtain diamide I in its glassy form. Interestingly diamides II and III with T_g 's at 65°C and 33°C, respectively, exhibit a T_g/T_m ratio of 0.65. Assuming a similar ratio for I, a T_g of 94°C is calculated. The higher T_g of diamide I compared to II can be related to its relatively rigid structure as a result of the conjugation of two *m*-carbonyls with the central benzene ring. The lowest T_g of diamide III can be attributed to the symmetrical substitution of two chlorine substituents and/or to the reduced intermolecular forces in the amorphous state.

Although no T_g could be detected upon heating the quenched diamide I, a small exotherm was observed at ~158°C. The latter may represent either a small crystallization or a reorganization

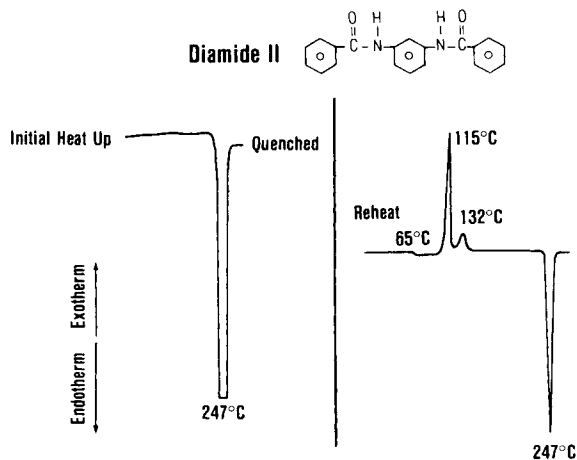


Fig. 2. Typical DSC thermograms of a crystalline and glassy aromatic diamide (sensitivity is four times lower for the reheat scan).

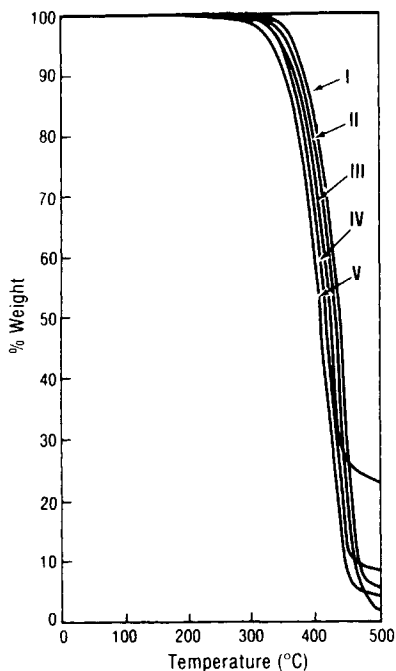


Fig. 3. TGA thermograms of the aromatic diamides in argon.

of the crystallites. Diamides II and III show a doublet crystallization when heated from the glassy state. Since both of them exhibit a single melting, it appears that the higher temperature exotherm is associated with reordering of the crystallites. Similar behavior is usually observed with amorphous alloys.⁴

Similarity of the melting points upon initial heatup (drying at 125°C/6 hr) and reheating the quenched diamides suggests that the melting behavior of these compounds is thermal history independent. This is to be expected from the low-molecular-weight materials.

Thermal Stability

Major degradation of these materials takes place in the 300–450°C range (Fig. 3). Based on the initial decomposition temperature (IDT), the temperature of the maximum rate of weight loss (T_{\max}), and the weight loss data in the 300–400°C range, the following thermal stability ranking can be established for these diamides:

$$I > II > III > IV > V$$

The highest stability of diamide I may be attributed to its stiffer and planar structure as a result of the conjugation of the central benzene ring with two *m*-carbonyl groups. Interestingly, the diamide IV forms the maximum char at 500°C, which indicates that a chlorine atom on a benzene ring containing two diamide groups is a desirable factor in increasing the char yield in aromatic polyamides.⁵

CONCLUSIONS

The phenomenon of glass transition, cold crystallization, and melting typical of semicrystalline and crystallizable polymers has been described for some aromatic diamides. Attempts are made to correlate the thermal transitions and stability of these diamides with their structures.

References

1. M. R. Carpenter, D. B. Davies, and A. J. Matheson, *J. Chem. Phys.*, **46**(7), 2451 (1967).
2. A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley, New York, 1968, p. 37.
3. Y. P. Khanna, E. M. Pearce, B. D. Forman, and D. A. Bini, *J. Polym. Sci., Polym Chem. Ed.*, **19**, 2795 (1981).
4. M. G. Scott, *J. Mater. Sci.*, **13**, 291 (1978).
5. Y. P. Khanna and E. M. Pearce, *J. Polym. Sci., Polym Chem. Ed.*, **19**, 2831 (1981).

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