

Melting Behavior of Aliphatic and Aromatic Diamides

INTRODUCTION

Aromatic polyamides form a special class of polymers which have high melting temperatures and yield fibers with very high Young's moduli.¹⁻³ The melting behavior of aliphatic, aliphatic-aromatic, and aromatic polyamides have previously been studied.³⁻⁶ In general it can be said that the melting temperature T_m increases with increasing aromaticity. Black and Preston³ suggest that an important role is played by the ability of a 1,4-substituted benzene unit in the polyamide chain to form a molecular arrangement which allows better intermolecular registration of the amide groups for hydrogen bonding. According to them, one must take into account the possible conjugation of the aromatic group with the amide group which results in the planarity of a larger segment. Aubineau,⁴ studying aliphatic-aromatic copolyamides, observed a considerable rise in T_m when phenyl groups were attached to both sides of the amide group. He explained the increase in T_m on increasing aromaticity from aliphatic to aliphatic-aromatic by the increase in molecular stiffness. The strong increase in T_m on increasing aromaticity from aliphatic-aromatic to aromatic systems is explained by a further increase in molecular stiffness of the polymer chain, the conjugation over the amide bond, and possibly also an increase in hydrogen bonding interaction. Recently Northolt⁷ reported the crystalline structure of poly-*p*-phenyleneterephthalamide. The hydrogen bond distance was found to be 3.04 Å, which is greater than the hydrogen bond distance⁸ in aliphatic polyamides (2.8 Å). This suggests that poly-*p*-phenyleneterephthalamide has weaker hydrogen bonding than the aliphatic polyamides.

As most of the reported properties of the semicrystalline polyamides depend on the not so well defined crystalline phase, it would be informative to look at simple model compounds. Therefore we studied the effects of substituting a 1,4-tetramethylene group for a 1,4-benzene group in diamides with either butyl or phenyl end groups.

EXPERIMENTAL

The diamides (Table I) were prepared from purified amines and acid chlorides⁹ and recrystallized from benzyl alcohol. The melting behavior was studied by DSC (Perkin-Elmer DSC-1B). The heating rate was 16°C/min. The onset of melting was taken as the melting point T_m . The heat of melting (ΔH_m) was obtained by integrating the melting curve with a Kipp integrator connected to the recorder, calibration of the apparatus being run against indium. The entropy of melting ΔS_m was calculated from the enthalpy of melting and the melting temperature:

$$\Delta S_m = \Delta H_m/T_m$$

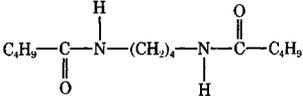
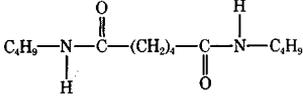
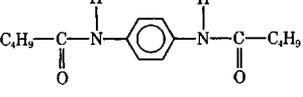
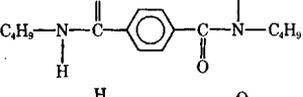
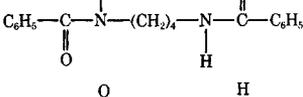
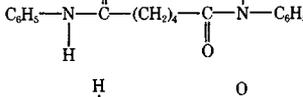
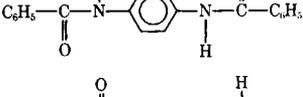
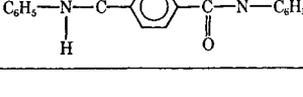
The thermal data obtained are presented in Table I and Figure 1.

RESULTS

The melting temperatures of the wholly aliphatic (I, II), aliphatic-aromatic-aliphatic (III, IV), and wholly aromatic-diamides (VII, VIII) are independent of the direction of the amide bonds. However, among the aromatic-aliphatic-aromatic diamides (V, VI), dianilinoadipamide (VI) has a higher melting temperature than tetramethylenebisbenzamide (V). The T_m of the diamides increased on substituting a 1,4-tetramethylene unit for a 1,4-benzene group. The largest increase in T_m is found when the diamide has phenyl end groups, in going from aromatic-aliphatic-aromatic (V, VI) to wholly aromatic compounds (VII, VIII). These results are in agreement with those obtained with aliphatic, aliphatic-aromatic, and wholly aromatic polyamides.⁴

The heats of melting (ΔH_m) of the wholly aliphatic and aliphatic-aromatic-aliphatic diamides (III, IV) are very similar. A greater difference exists between V and VI and also VII and VIII. Such differences in ΔH_m may be due to a change in molecular interactions, probably as a result of different chain packings.¹⁰ In going from wholly aliphatic (I, II) to aliphatic-aromatic-aliphatic (III, IV),

TABLE I
 Melting Data for Diamides

No.	Symbol ^a	Diamide	Molecular weight	T_m , °C	ΔH_m , kcal/mole	ΔS_m , cal/mole-°K
I	▼		256	143	8.0	19.5
II	■		256	170	8.5	19.5
III	▽		276	231	8.0	16.0
IV	□		276	228	8.0	16.5
V	△		296	180	11.0	24.0
VI	○		296	241	12.5	24.5
VII	▲		316	343	15.0	24.5
VIII	●		316	344	17.0	27.5

^a See Fig. 1.

ΔH_m remains constant. However, ΔH_m increases strongly in going from aromatic-aliphatic-aromatic (V, VI) to wholly aromatic diamides (VII, VIII). This increase is hard to explain, as one would not expect a closer packing in the amide plane. Possibly, this increase in ΔH_m is due to π - π interactions. The entropy of melting (ΔS_m) is very similar for I and II, III and IV, and V and VI. The ΔS_m of VII and VIII show a marked difference which has not been explained yet.

The ΔS_m decreased in going from wholly aliphatic to aliphatic-aromatic-aliphatic. This must be due to the chain-stiffening effect of incorporating a benzene unit in the diamides. In going from aromatic-aliphatic-aromatic to wholly aromatic, the ΔS_m increases slightly. It had been expected that ΔS_m would decrease due to a further increase in molecular stiffness as a result of an increase in aromaticity and possible conjugation.

CONCLUSION

The melting temperatures of the diamides increase with increasing aromaticity, as in the aliphatic, aliphatic-aromatic, and aromatic polyamides.⁴ This increase is strongest when the 1,4-tetramethylene is substituted for a 1,4-benzene unit in diamide with phenyl end groups.

The increase in T_m from wholly aliphatic (I, II) to aliphatic-aromatic-aliphatic (III, IV) is due

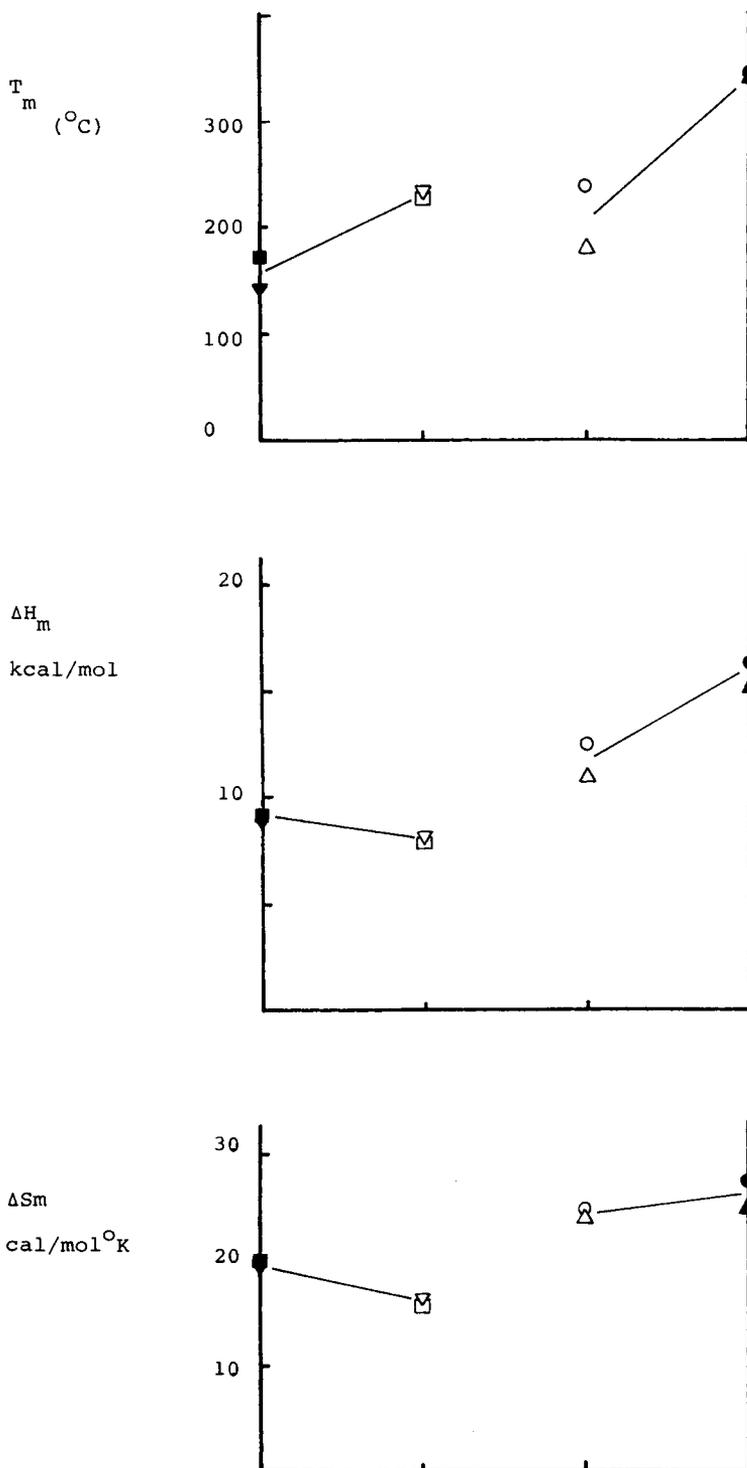


Fig. 1. Melting behavior of diamides: (\blacktriangledown) I and (\blacksquare) II, wholly aliphatic; (∇) III and (\square) IV, aliphatic-aromatic-aliphatic; (\triangle) V and (\circ) VI, aromatic-aliphatic-aromatic; (\blacktriangle) VII and (\bullet) VIII, wholly aromatic diamides.

solely to a decrease in ΔS_m , which results from the chain stiffening due to incorporation of a benzene unit in the diamide. The strong increase in T_m from aromatic-aliphatic-aromatic (V, VI) to wholly aromatic compounds (VII, VIII) seems to be due to the high heats of fusion of the wholly aromatic compounds.

The conjugation which is expected to take place in the aromatic polyamides^{3,4} does not seem to take place in these aromatic diamides. Conjugation reduces the intermolecular interaction and thus both ΔH_m and ΔS_m . Neither effect seems to take place between the aromatic-aliphatic-aromatic (V, VI) and the wholly aromatic diamides (VII, VIII).

References

1. J. H. Rothuizen, *Text. Inst. Ind.*, **11**, 142 (1973).
2. R. E. Wilfong and J. Zimmerman, *J. Appl. Polym. Sci.*, **17**, 2039 (1973).
3. J. Preston and W. B. Black, in *Man-Made Fibers*, H. F. Mark, S. M. Atlas, and E. Cernia, Eds., Vol. 2, Interscience, New York, 1968, p. 365.
4. C. Aubineau, R. Audebert, and G. Champetier, *Bull. Soc. Chim. France*, **1970**, 1404.
5. P. W. Morgan and S. L. Kwolek, *Macromolecules*, **8**, 104 (1975).
6. T. C. Tranter, *J. Polym. Sci. A*, **2**, 4289 (1964).
7. M. G. Northolt, *Eur. Polym. J.*, **10**, 799 (1974).
8. C. W. Bunn and E. V. Garner, *Proc. Roy. Soc. (London)*, **A189**, 39 (1948).
9. A. I. Vogel, *Practical Organic Chemistry*, 32rd ed., Longmans, London, 1956, p. 361.
10. A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley, New York-London, 1968, p. 139.

R. J. GAYMANS
S. HARKEMA

Department of Chemical Technology
Twente University of Technology
P.O. Box 217
Enschede, The Netherlands

Received August 24, 1976