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MELTING BEHAVIOUR OF A SERIES OF MONOAMIDES

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ABSTRACT

The melting behaviour of the monoamides of general formula (n-C_pH_{2p+1})CONH-(n-C_qH_{2p+1}) is investigated by differential scanning calorimetry (DSC) and infrared spectroscopy. The lower values of melting entropies, compared to those for linear hydrocarbons with the same number of conformationally flexible chain bonds, is attributed to a reduction in the number of conformations available to the hydrocarbon portion of the molecule, because of the large amount of hydrogen bonding maintained in the melt. The melting behaviour of the monoamides is compared with that of the diamides discussed in a previous paper [1]. The persistence of a network of hydrogen bonds in the melt of the diamides reduces the conformational freedom of the chain segments more than for the monoamides.

INTRODUCTION

In a previous paper [1] we reported the melting data of a series of diamides of variable chain length. The lower melting entropies and the higher melting temperatures, compared to those of linear hydrocarbons with the same number of conformationally flexible bonds, were attributed to a reduction of conformational freedom of the chain segments in the liquid state, owing to the large fraction of hydrogen bonds maintained in the melt. Results of a calorimetric and spectroscopic investigation of the melting behaviour of monoamides of general formula (n-C_pH_{2p+1})CONH(n-C_qH_{2q+1}) is reported in this paper. Monoamides will be denoted as C_pC_q for convenience.

EXPERIMENTAL

The monoamides were prepared according to the following typical method. The monoamine (0.2 mole) was dissolved in 300 ml of $CHCl_3$. The solution was cooled in an ice/salt bath and acyl chloride (0.1 mole) was added dropwise with stirring. After 1 h the mixture was allowed to warm to room temperature, left under stirring for 6 h, dried in vacuo and the solid residue poured into a saturated $NaHCO_3$ solution. After further washings with water, the residue was dried and recrystallized from an ethyl alcohol/ ethyl acetate solution. The relative amount of ethyl alcohol was increased with increasing molecular weight of the product. The purity of product was checked by elemental analysis, thin layer chromatography (eluant pentane/ benzene 1 : 10), IR, and NMR. The calorimetric melting behaviour of all the prepared compounds was investigated with a Perkin-Elmer DSC-1 differential scanning calorimeter, at a scanning rate of 16 K min^{-1} in an N_2 atmosphere.

The temperature scale was calibrated using pure reference compounds. Transition and melting enthalpies were obtained with a weighed indium sample ($\Delta H = 28.5$ J g^{-1}) as reference standard. The reported transitions and melting enthalpies are mean values of several independent determinations. For each set of measurements the standard deviation is about 4%.

IR spectra were taken with a Perkin-Elmer 457 apparatus equipped with a variable-temperature sample cell. Samples were prepared by melting the finely powdered compounds between KBr windows. Sample thicknesses were about 0.05 mm.

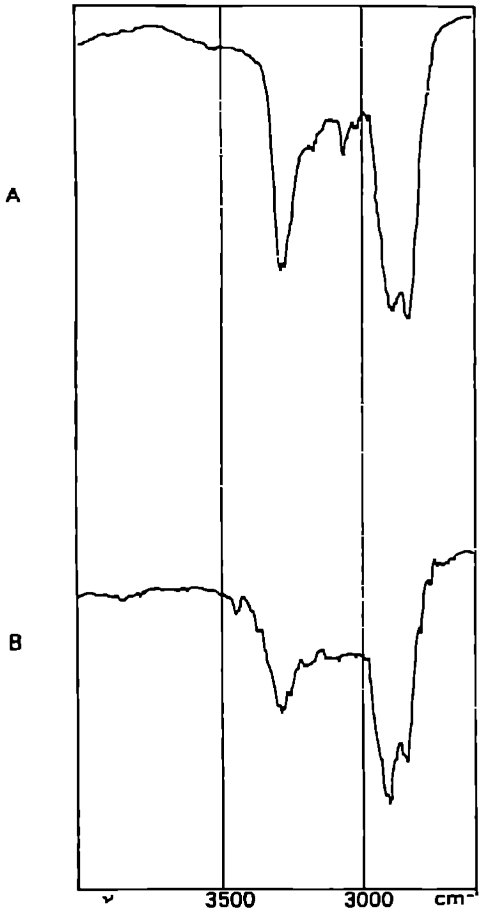

Fig. 1. Part of the IR spectra of the C_9C_6 monoamide at 298 K (A) and 323 K (B).

TABLE 1

Values of $\mu = E_b/(E_b + E_f)$ showing the retention of hydrogen bonds in the melt of the C_9C_6 monoamide (T_m = 311 K)

T (K)	μ (%)
298	100
323	80

RESULTS

All the monoamides investigated melted without decomposition in the range 300—350 K. Some also showed solid—solid phase transitions in the investigated range of temperatures.

The transition and melting behaviour of all the monoamides was reproducible in respect of both temperature and enthalpy, over several heating DSC scans.

Figure 1 shows the low- and high-temperature IR spectra of the C_9C_6 monoamide in the region 4000—2600 cm^{-1}. We have calculated the fraction of N—H groups which are engaged in hydrogen bonds, following the method outlined by Bessler and Bier [2] for Nylon 6,6. Table 1 shows the values of the ratio $\mu = E_b/(E_b + E_f)$, obtained from the spectra, where E_f and E_b are the intensities of the non-hydrogen-bonded (3450 cm^{-1}) and hydrogen-bonded (3320 cm^{-1}) N—H stretching bands, respectively. It is seen that a very large fraction of the hydrogen bonding present in the crystals is retained in the molten monoamides. The percentage retention is about 80%.

DISCUSSION

Figure 2 shows that the total transition and melting entropies (ΔS_t) of the monoamides are always lower than those of the linear hydrocarbons with the same number of conformationally flexible chain bonds *, but are higher than those of the corresponding diamides. This is not surprising because the retention of hydrogen bonds in the molten monoamides, while hindering the relative mobility of the molecules, does not deny as large a set of conformations to the hydrocarbon portions of the molecules as in the case of the molten diamides [3]. A further indication that this is so comes from the conformational term of the melting entropy, which may be calculated in the rotational isomeric approximation [4] if the molecules in the melt are free to assume conformations unconstrained by the hydrogen bonds. The maximum limiting conformational entropy (under the assumption that complete conformational freedom is acquired by the *n*-hydrocarbon molecules on melting [4]) corresponds in the case of linear hydrocarbons to a fraction of

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* The number of conformationally flexible chain bonds in a C_pC_q monoamide is $p + q$ — 2.

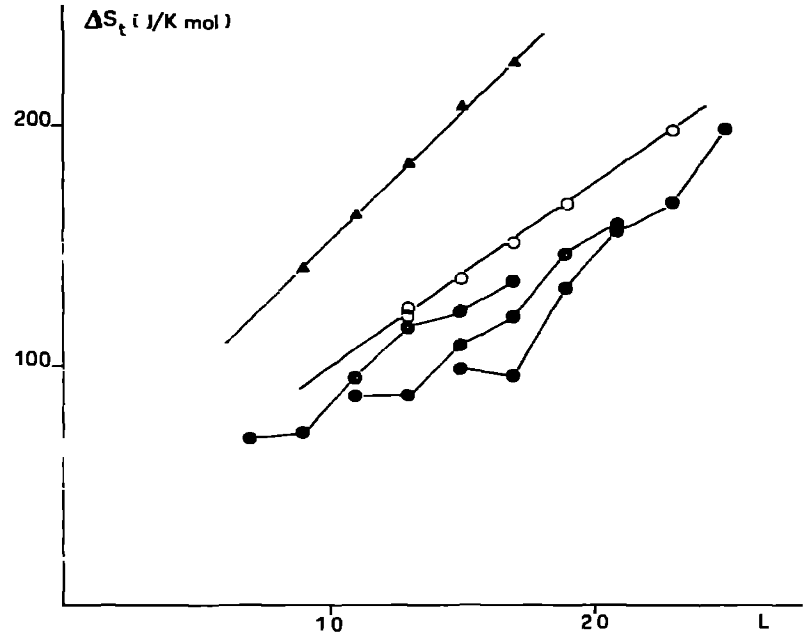

Fig. 2. Plot of the total transition and melting entropy of diamides (●), monoamides ( ), and linear hydrocarbons (▲) versus the number L of conformationally flexible chain bonds.

ΔS_t which ranges from 46% for n-undecane [5—7] to the value of 77% calculated by Tonelli [8] for polyethylene. As we have already pointed out [1], the conformational entropy of the "free molecules" calculated for the diamides is, in contrast, of the order of ΔS_t or even higher. The situation, as expected, is intermediate for the monoamides. In fact, as can be seen from

TABLE 2

Transition and melting data of monoamides $(n\text{-}C_pH_{2p+1})CONH(n\text{-}C_qH_{2q+1})$ (short notation C_pC_q) with various values of p and q *

Mono-amide	T_{tr} (K)	T_m (K)	ΔH_{tr} (kJ mole^{-1})	ΔH_m (kJ mole^{-1})	ΔS_{tr} (J K^{-1} mole^{-1})	ΔS_m (J K^{-1} mole^{-1})	ΔS_{conf} (J K^{-1} mole
C_9C_6	301	311	6	31	20	100	95
$C_{11}C_4$		322		39		122	96
$C_{13}C_4$		336		45		135	110
$C_{13}C_6$	310,328	334	8,7	35	25,20	105	124
$C_{15}C_6$		343		57		166	139
$C_{15}C_{10}$	333	347	5	63	15	182	168

* T_{tr}, T_m, ΔH_{tr}, ΔH_m, ΔS_{tr}, ΔS_m = transition temperature, melting temperature, transition enthalpy, melting enthalpy, transition entropy and melting entropy, respectively. ΔS_{conf} = conformational contribution to the total transition and melting entropy, calculated using the rotational isomeric approximation under the assumption of complete conformational freedom of the chains in the liquid at the melting point.

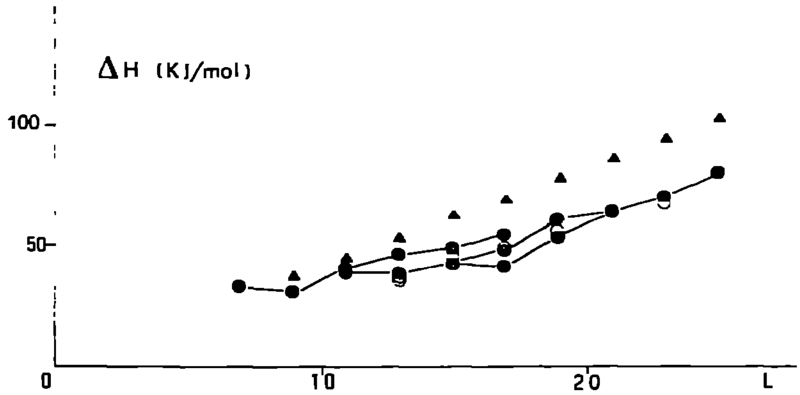

Fig. 3. Plot of the total transition and melting enthalpy of diamides (●), monoamides (○), and linear hydrocarbons (▲) versus the number L of conformationally flexible chain bonds.

Table 2, the conformational entropy of the "free molecules" is about 80—85% of the total melting entropy. On the other hand, as can be seen from Fig. 3, the total melting enthalpies of the monoamides are only slightly lower than those of the corresponding linear hydrocarbons, but are of the same order of magnitude of the corresponding diamides. As a result, the melting points $T_m = \Delta H_m / \Delta S_m$ of the monoamides (Fig. 4) are slightly above those of the corresponding hydrocarbons and substantially below those of the corresponding diamides.

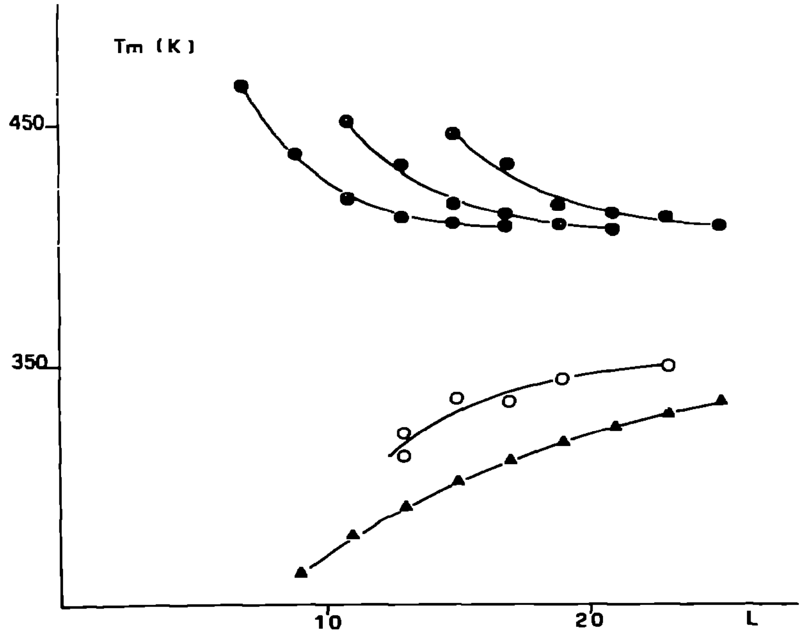

Fig. 4. Plot of the melting temperature of diamides (●), monoamides (○), and linear hydrocarbons (▲) versus the number L of conformationally flexible chain bonds.

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