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MELTING BEHAVIOUR OF A SERIES OF DIAMIDES

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ABSTRACT

The melting behaviour of diamides of general formula $(n - C_pH_{2p+1})CONH(CH_2)_qNHCO(n - C_pH_{2p+1})$ has been investigated by calorimetric, dilatometric and IR techniques. The conformational contribution to the melting entropy, calculated from the hypothesis of complete conformational freedom of the molecules at the melting point, has been compared with the experimental data. The higher melting points of the diamides, as compared with those of the linear hydrocarbons having the same number of conformationally flexible chain bonds, are attributed to a reduction of conformational freedom of the chain segments in the liquid state (caused by the large fraction of hydrogen bonds maintained in the melt).

INTRODUCTION

It is well known that a large fraction of the melting entropy of long chain hydrocarburic substances is due to the liberation at the melting point of rotations about the conformationally flexible chain bonds[1]. The experimental data, relatively abundant in the case of linear hydrocarbons, have been successfully compared with the results of calculations, assuming in the melt the same conformational freedom of the chains as in the unperturbed gaseous state[5]. Much less is known, from the systematic viewpoint, in the case of molecules in which directional intermolecular interactions may reduce the conformational freedom of the chain segments in the melt. Such interactions could be provided, for instance, by hydrogen bonds.

We wish to report in this paper complete results of a calorimetric, dilatometric and spectroscopic investigation of the melting behaviour of diamides of general formula $(n - C_pH_{2p+1})CONH(CH_2)_qNHCO(n - C_pH_{2p+1})$ with various values of p and q. Diamides will be denoted as $C_pC_qC_p$ for convenience.

Some preliminary data, relevant to the explanation of the melting behaviour of polyamides, have already been published[2].

EXPERIMENTAL

Diamides were prepared according to the following general method. In a typical preparation 0.1 mole of diamine was dissolved in 300 ml of $CHCl_3$ with 0.2

mole of pyridine. The solution was cooled in an ice: salt bath and 0.2 mole of acyl chloride was added dropwise with stirring. After 1 h, the mixture was allowed to warm to room temperature and left under stirring for 6 h. The mixture was then dried in vacuo and the solid residue poured in 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 products. The purity of the products was checked by elemental analysis, thin layer chromatography (eluent pentane/benzene 1: 10), IR, NMR and mass spectroscopy.

The calorimetric melting behaviour of all the prepared compounds has been investigated using a Perkin-Elmer DSC-1 differential scanning calorimeter, at the scanning rate of 16 K min^{-1} in a N_2 atmosphere. The temperature scale was calibrated using pure reference compounds. The transition and melting enthalpies were obtained using as a reference standard a weighed indium sample (ΔH = 28.5 J g^{-1}). The reported transition and melting enthalpies are mean values of various independent determinations. For each set of measurements, the standard deviation is of the order of 4%.

Dilatometric curves were obtained using dilatometers similar to that described by Danusso et al.[3]. After calibration and sample introduction, the apparatus was filled with mercury by suction at a pressure of 10^{-3} Torr. The system was allowed to equilibrate at each increasing temperature before determination of the meniscus height with a cathetometer.

IR spectra were taken with a Perkin-Elmer 125 apparatus equipped with a variable temperature sample cell. Samples were prepared by melting the finely powdered compounds between NaCl windows. Sample thicknesses were of the order of 0.05 mm.

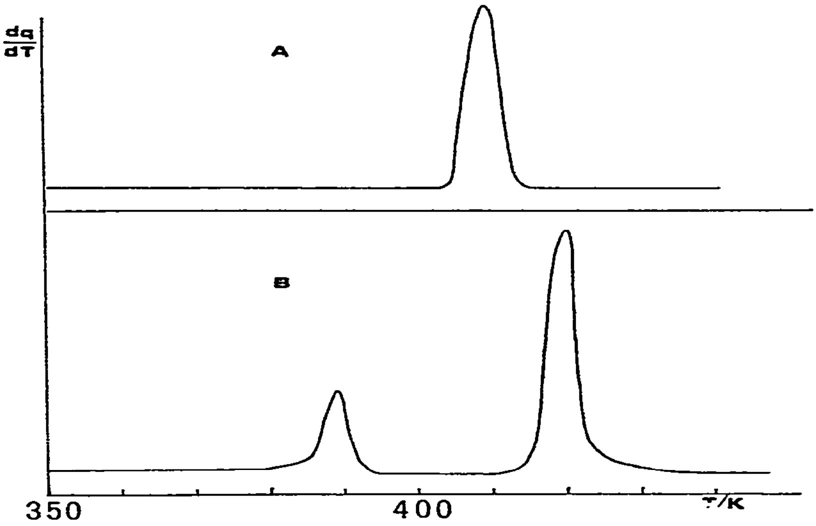

Fig. 1. Portion of typical heating thermograms of the $C_7C_{10}C_7$ (A) and $C_3C_6C_3$ (B) diamides.

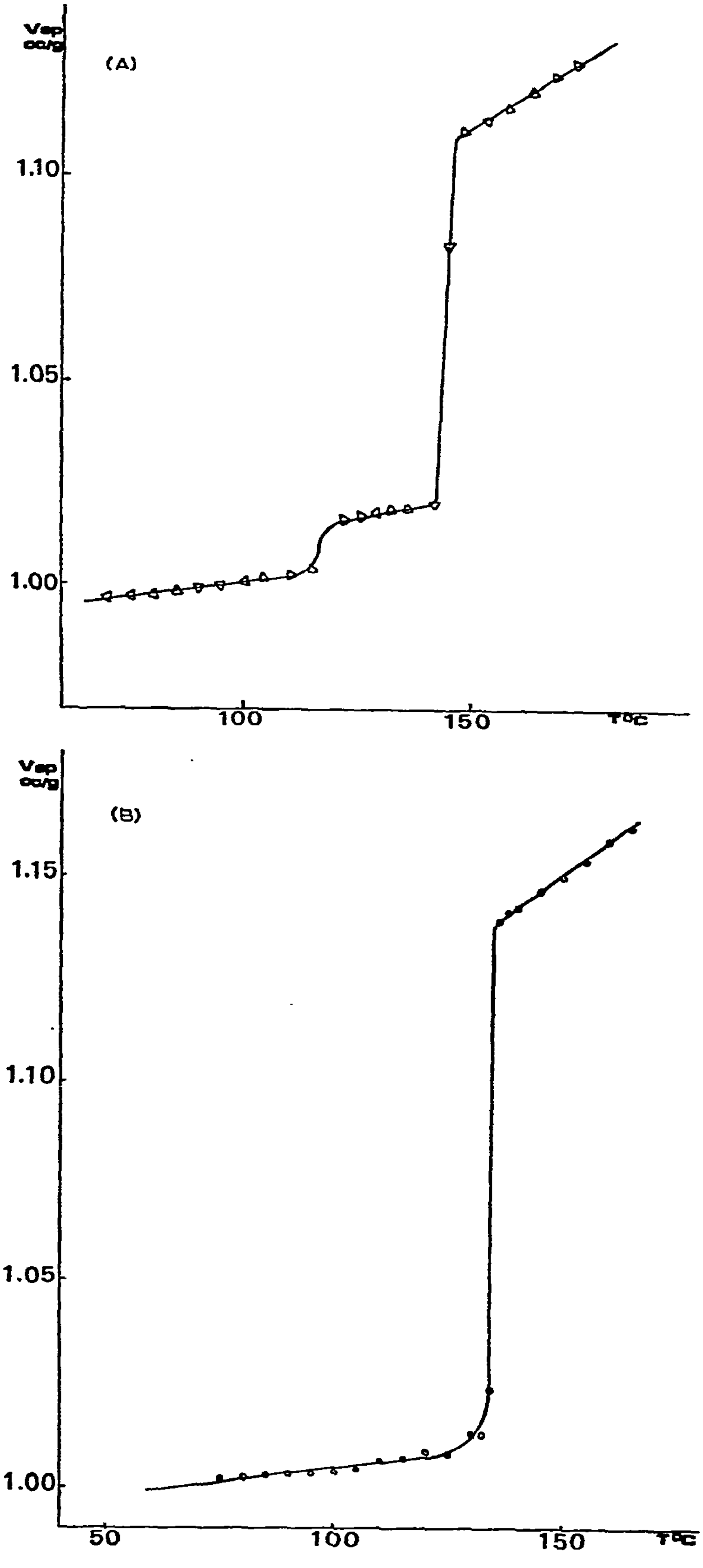

Fig. 2. Dilatometric curves obtained in the case of the $C_3C_6C_3$ (A) and $C_7C_{12}C_7$ (B) diamides.

TABLE 1

TRANSITION AND MELTING DATA OF DIAMIDES $(n\text{-}C_pH_{2p+1})CONH(CH_2)_qNHCO(n\text{-}C_pH_{2p+1})$ (SHORT NOTATION $C_pC_qC_p$) WITH VARIOUS VALUES OF p AND q

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

Diamide	T_{tr} *(K)*	T_m *(K)*	ΔH_{tr} *(KJ/mole)*	ΔH_m *(KJ/mole)*	ΔS_{tr} *(J/K mole)*	ΔS_m *(J/K mole)*	ΔV_{tr} *(cm³/mole)*	ΔV_m *(cm³/mole)*	ΔS_{conf} *(J/K mole)*
$C_3C_2C_3$		465		33		70			59
$C_3C_4C_3$	380	437	4	27	11	61			74
$C_3C_6C_3$	390	420	10	30	26	69	3.1	21.0	88
$C_5C_2C_5$		451		39		87		28.2	88
$C_3C_8C_3$	393	412	11	36	29	87	1.4	25.6	102
$C_5C_4C_5$		433		38		88			103
$C_3C_{10}C_3$	395	409	11	38	28	94			117
$C_7C_2C_7$		446		44		98			117
$C_5C_6C_5$	406	417	6	39	14	94			117
$C_3C_{12}C_3$	396	407	7	48	17	117	2.0	41.5	131
$C_5C_8C_5$		412		49		120			132
$C_7C_4C_7$		446		41		95			132
$C_5C_{10}C_5$		408		60		146			146
$C_7C_6C_7$		417		55		132			146
$C_5C_{12}C_5$		407		64		158			160
$C_7C_8C_7$		413		64		155		54.2	161
$C_7C_{10}C_7$		411		69		167			171
$C_7C_{12}C_7$		407		81		198		57.8	190

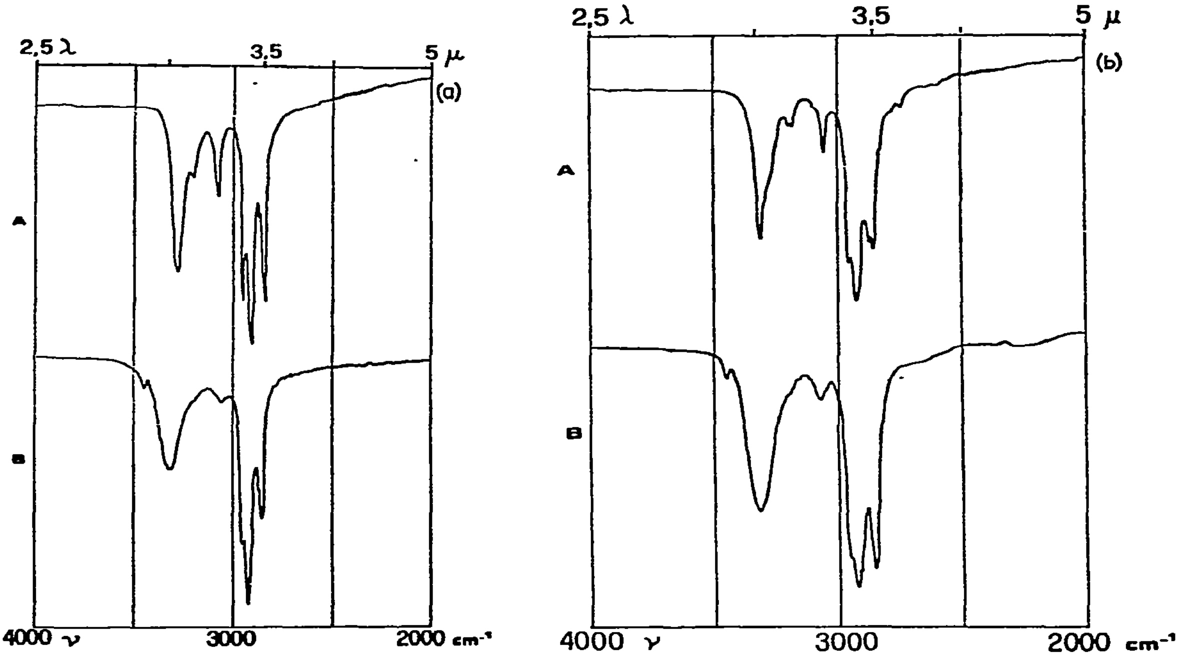

Fig. 3. Portion of interest of the IR spectra of the $C_7C_2C_7$ diamide (a) at room temperature (A) and at 195 °C (B), and of the $C_7C_8C_7$ diamide (b) at room temperature (A) and at 160 °C (B).

TABLE 2

VALUES OF $\mu = E_b/(E_b + E_f)$ (SEE RESULTS) SHOWING THE RETENTION OF HYDROGEN BONDING IN THE MELT OF TWO DIAMIDES

T	μ
(K)	(%)
$C_7C_2C_7$ (T_m = 446 K)	
303	100
403	100
447	87
468	87
$C_7C_8C_7$ (T_m = 413 K)	
303	100
363	100
415	89
420	88
429	88

RESULTS

All the diamides investigated in this work melt without decomposition in the range 380–470 K. Some of them show also solid–solid phase transitions in the investigated range of temperatures. Figure 1 shows the portion of interest of typical heating thermograms of some representative compounds. The transition and melting behaviour of all the diamides is always reproducible both in temperature and enthalpy, after various heating DSC scans.

We have investigated the volume/temperature behaviour near the transition and melting points of a number of compounds. Figure 2 shows the dilatometric curves obtained in the case of the $C_3C_6C_3$ and $C_7C_{12}C_7$ diamides. Table 1 shows the volume increments at the transition and the melting points for some diamides.

Figure 3 shows the low and high temperature IR spectra of the $C_7C_2C_7$ and $C_7C_8C_7$ diamides in the region 3500/2500 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[4] for nylon 6,6. Table 2 shows the values of the ratio $\mu = E_b/E_b + E_f)$ obtained from the previous 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 band, respectively. It may be seen that, not unexpectedly, a very large fraction of the hydrogen bonds present in the crystals is retained also in the molten diamides at the melting point, the percentage retention being of the order of 90%.

CALCULATION

The scope of this section is to refer to calculations performed by us in order to estimate the conformational freedom which would be acquired in the melt by the diamide molecules if hydrogen bonds were not present. We have also performed analogous calculations in the case of linear hydrocarbons, in which directional intermolecular interactions are absent. By comparing the two sets of calculated values with the experimental melting entropy of the diamides, it will be possible, in the discussion section, to estimate the influence that the retention of hydrogen bonds has on the conformational freedom of the diamide molecules in the melt.

The conformational contribution to the melting entropy of long chain molecules can be evaluated by standard statistical thermodynamics[9] as $\Delta S_{\text{conf}} = R\ln Z + R\text{d}\ln Z_c/\text{d}\ln T$, where Z_c is the conformational partition function at the melting point. Z_c and its temperature coefficient can be calculated under the assumption that the chain can assume in the melt the whole set of conformations which would be available for an isolated molecule unperturbed by long-range self-interactions[5, 9].

For unbranched n-bond molecules, in the three state rotational isomeric approximation[5]

$$Z_c = X^* \left[\prod_{i=2}^{n-1} U_i \right] X$$

where X^* is the row vector $|1\ 0\ 0|$. X is the column vector

$$\begin{vmatrix} 1 \\ 1 \\ 1 \end{vmatrix} \text{ and } U_i = \begin{vmatrix} 1 & \sigma_i & \sigma_i \\ 1 & \sigma_i & \sigma_i\omega_i \\ 1 & \sigma_i\omega_i & \sigma_i \end{vmatrix}$$

TABLE 3

TRANSITION AND MELTING DATA OF LINEAR HYDROCARBONS(6–8)

T_{tr}, T_m, ΔS_{tr}, ΔS_m, ΔV_{tr}, ΔV_m, ΔS_{conf} = transition and melting temperature, transition and melting entropy, transition and melting volume expansion and calculated conformational contribution to the melting entropy.

n-Alkane	T_{tr} (*K*)	T_m (*K*)	ΔS_{tr} (*J/K mole*)	ΔS_m (*J/K mole*)	ΔV_{tr} (*cm³/mole*)	ΔV_m (*cm³/mole*)	ΔS_{conf} (*J/K mole*)
C_{11}	237	248	29	89	8.27	19.19	54
C_{12}		264		140		34.68	61
C_{13}	255	268	30	106	8.28	26.49	69
C_{14}		279		162		41.98	76
C_{15}	271	283	34	122	9.12	27.98	83
C_{16}		291		183		45.65	90
C_{17}	284	295	38	136	11.52	32.64	97
C_{18}		301		208		52.83	104
C_{19}	296	305	47	150	14.20	37.52	111
C_{20}	309	310		225		58.66	118
Polyethylene	410			9.6*		6.13*	7.4*

* J/K mole of monomer.

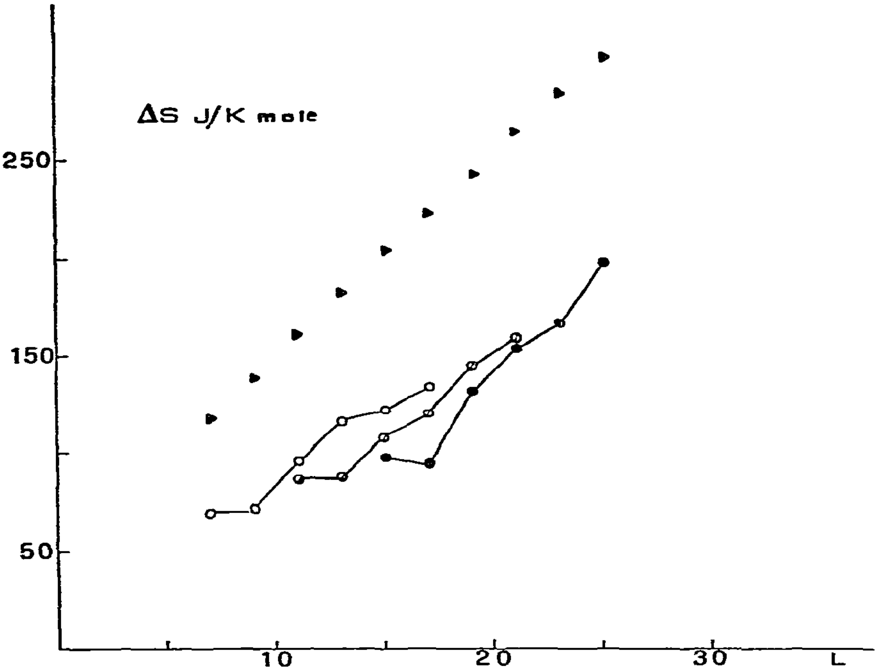

Fig. 4. Plot of the total transition and melting entropy of diamides and linear hydrocarbons versus the number, L, of conformationally flexible chain bonds. ▲, Linear hydrocarbons[6-8]; ●, diamides with $p = 7$; ⊖, diamides with $p = 5$; ○, diamides with $p = 3$.

$\sigma_i = \exp(-E_{g,i}/RT)$ and $\omega_i = \exp(-E_{\omega,i}/RT)$ are statistical factors associated with rotations about the *i*th chain bond.

Table 3 shows literature values of the melting entropy of a series of linear hydrocarbons, along with values of ΔS_{conf} calculated by us in the previous approximation with $E_{g,i} = E_g = 2100$ J mole^{-1} and $E_{\omega,i} = E_\omega = 700$ J mole^{-1}. The last column of Table 1 shows ΔS_{conf} values calculated for the diamides using the $E_{g,i}$ and $E_{\omega,i}$ reported by Flory[5] for the corresponding bonds of polyamides. These values, calculated for unperturbed isolated molecules, represent the maximum limiting conformational entropy which would be obtained if no intermolecular interaction were present.

DISCUSSION

Figure 4 shows that the total transition and melting entropies (ΔS_t) of the linear hydrocarbons are always considerably higher than those of diamides having the same number of conformationally flexible chain bonds*. In our view, this fact suggests that the conformational freedom acquired by the diamide molecules on melting is lower than the corresponding freedom of the linear hydrocarbons. A further indication that

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* The number of conformationally flexible chain bonds in a $C_pC_qC_p$ diamide is $2p + q - 1$, while it is $n - 3$ in a linear C_nH_{2n+2} hydrocarbon.

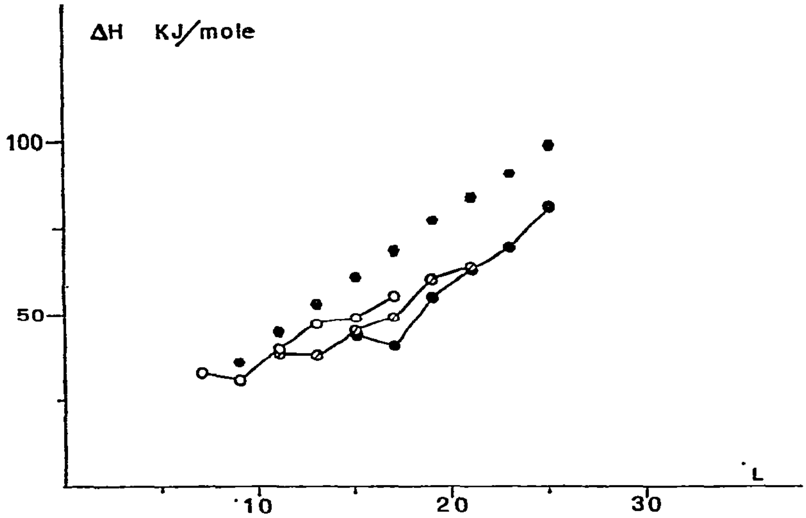

Fig. 5. Plot of the total transition and melting enthalpy of diamides and linear hydrocarbons, versus the number, L, of conformationally flexible chain bonds. ©, Linear hydrocarbons[6-8]; ●, diamides with $p = 7$; ⊖, diamides with $p = 5$; ○, diamides with $p = 3$.

it may be so comes from the calculations of the previous section. The maximum limiting conformational entropy (Table 3) corresponds, in the case of the linear hydrocarbons, to a fraction of ΔS_t which goes from a value of 46 % for the n-undecane to a value of 77 %, calculated by Tonelli[9], for polyethylene. It is generally assumed[5] that an almost complete conformational freedom is acquired by n-hydrocarbons on melting.

The situation seems to be quite different if we consider the diamides. In fact, the maximum conformational entropy, calculated from the hypothesis of complete conformational freedom in the melt, is in this case of the same order of ΔS_t, or even higher, while it should be only a part of ΔS_t (ref. 9). This observation indicates that a complete conformational freedom is not acquired by the diamide molecules on melting. We suggest that this is mainly due to the high retention of hydrogen bonds in the melt

TABLE 4

TOTAL TRANSITION AND MELTING VOLUME EXPANSION OF VARIOUS DIAMIDES AND LINEAR HYDROCARBONS$^{(6-8)}$ HAVING THE SAME NUMBER OF CONFORMATIONALLY FLEXIBLE BONDS

Diamide	*ΔV_{tr} (cm^3/mole)*	*ΔV_m (cm^3/mole)*	*n-Alkane*	*ΔV_{tr} (cm^3/mole)*	*ΔV_m (cm^3/mole)*
$C_5C_2C_5$		28.2	C_{14}		42.0
$C_3C_6C_3$	3.1	21.0			
$C_3C_8C_3$	1.4	25.6	C_{16}		45.6
$C_3C_{12}C_3$	2.0	41.5			
$C_7C_8C_7$		54.2	C_{24}	28.0	42.9
$C_7C_{12}C_7$		57.8	C_{28}	30.5	52.4

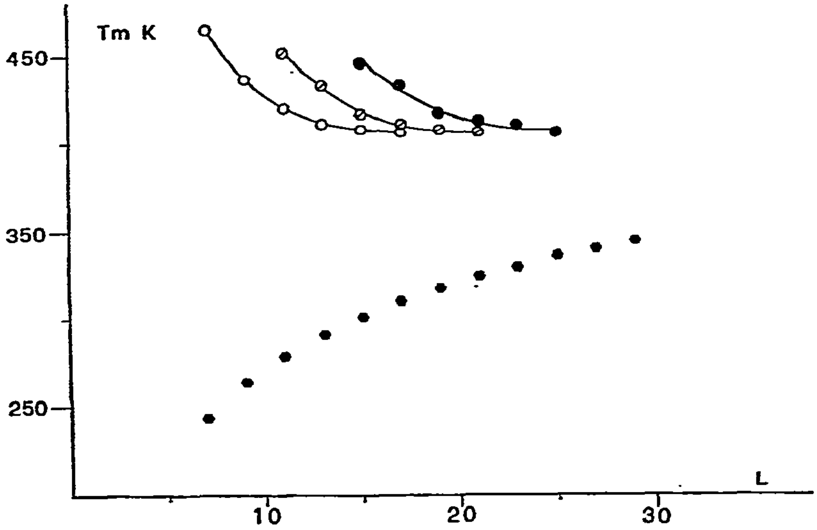

Fig. 6. Plot of the melting temperature of diamides and linear hydrocarbons, versus the number, L, of conformationally flexible chain bonds. ●, Linear hydrocarbons[6–8]; ●, diamides with $p = 7$; ⊖, diamides with $p = 5$; ○, diamides with $p = 3$.

(see Results), which precludes the diamide molecules from assuming the whole set of conformations which would be assumed if extended hydrogen bond networks were not present.

In Fig. 5, we compare the total melting and transition enthalpies (ΔH_t) of the diamides investigated in this work with those of the linear hydrocarbons. We also plot ΔH_t against the number of conformationally flexible bonds, in order to make easier the comparison with the corresponding plot of ΔS_t (Fig. 4). It is seen that the ΔH_t values for the diamides (as well as the ΔV_t values reported in Table 4) are always slightly lower than those of the hydrocarbons.

Thus, the higher melting point $T_m = \Delta H_m/\Delta S_m$ of the diamides, in comparison with the melting point of the corresponding hydrocarbons (Fig. 6) may be soundly correlated to the large lowering of the melting entropy, which is consequent to the preclusion, in the melt, of a large set of conformations to the hydrocarburic portions of the molecules considered.

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REFERENCES

1 P. Corradini, *J. Polym. Sci. Polym. Symp.*, 50 (1975) 327.
2 C. Carfagna, M. Vacatello and P. Corradini, *J. Polym. Sci.*, 15 (1977) 1.
3 F. Danusso, G. Moraglio, W. Ghiglia, L. Motta and G. Talamini, *Chim. Ind. (Milan)*, XLI (8) (1958) 748.
4 V. E. Bessler and G. Bier, *Makromol. Chem.*, 122 (1969) 30.
5 P. J. Flory, *Statistical Mechanics of Chain Molecules*, Interscience, 1969, p. 68.

6 A. A. Schaerer, C. J. Busso, A. E. Smith and L. B. Skinner, *J. Am. Chem. Soc.*, 77 (1955) 2017, and references therein.
7 J. F. Messerly, G. B. Guthrie, S. S. Todd and H. L. Pinke, *J. Chem. Eng. Data*, 12 (1967) 338, and references therein.
8 H. L. Finke, M. E. Gran, G. Waddington and H. M. Huffman, *J. Am. Chem. Soc.*, 76 (1954) 333, and references therein.
9 A. E. Tonelli, *J. Chem. Phys.*, 52 (1970) 4749.