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Analysis of the chainlength dependence of lipid phase transition temperatures: main and pretransitions of phosphatidylcholines; main and non-lamellar transitions of phosphatidylethanolamines

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The dependence on chainlength, n, of the temperatures at which the various thermotropic phase transitions in phospholipid bilayers take place can be fitted to high accuracy with an expression of the form: $T_t = T_t^\infty(1 - A/(n-d))$ where T_t^∞, A and d are the constants to be fitted. This expression works well with literature values for the main and pretransitions of saturated straight-chain phosphatidylcholines, for the main transition of isobranched- and anteiso-branched-chain phosphatidylcholines, and for the main and non-lamellar phase transitions of saturated straight-chain phosphatidylethanolamines, and also for diacylglycerol glycolipids. The parameters in the fit can be related thermodynamically to the calorimetric properties of the phase transition. The constants A and d are related to the end effects in the chainlength dependence of the transition enthalpy and transition entropy, respectively, and the transition temperature extrapolated to infinite chainlength, T_t^∞, is determined by the ratio of the incremental transition enthalpy and transition entropy per methylene group. A reasonable correspondence is found between the chainlength dependence of the transition temperature and of the transition enthalpy and transition entropy for saturated straight-chain diacylphosphatidylcholines. It is likely, however, that the expression for the chainlength dependence of the transition temperature may be of more general applicability, because, on the one hand of the greater inherent precision of the transition temperature measurements, and on the other hand because the expression for the transition temperature is of more general validity, provided that the chainlength dependence of the incremental transition enthalpy and entropy are the same.

Introduction

The chainlength dependence of the transition temperatures of diacyl phospholipids becomes less marked with increasing chainlength, as the contributions of the chains to the thermodynamics of the transition come to dominate over those of the lipid headgroups (see, e.g., Ref. 3). On the one hand, the predictive properties of an analytical expression for the chainlength dependence can be very useful in cases where experimental data is not available, and also in cases for which the experimental situation is complicated by phase metastability (see, e.g., Refs. 1 and 2). On the other hand, it is of considerable interest, both from a practical and an experimental point of view, to test whether such analytical descriptions may also be applied to lipid phase transitions other than the main chain melting transition, for example the pretransition of phosphatidylcholines and the lamellar to non-lamellar phase transitions of phosphatidylethanolamines.

In the present work, we have tested critically the validity of a theoretical description for an extensive series of measurements on the gel-to-fluid phase transitions of symmetrical disaturated phosphatidylcholines

Abbreviations: PC, phosphatidylcholine; PE, phosphatidylethanolamine; ester, 1,2-diacyl; ether, 1,2-dialkyl; isoacyl, 1,2-di[(ω-1)-methyl]acyl; anteiso, 1,2-di[(ω-2)-methyl]acyl; (n, n+6), 1-(n:0)-2-(n+6:0)-*sn*; ω-*t*-bu, 1,2-di[ω-*tert*-butyl]acyl; ω-cych, 1,2-di[ω-cyclohexyl]acyl; α-D-Glc-DAG, 1,2-diacyl-3-(α-D-glucopyranosyl)-*sn*-glycerol; β-D-Glc-DAG, 1,2-diacyl-3-(β-D-glucopyranosyl)-*sn*-glycerol; T_t, chain melting transition temperature (L_β-L_α, $L_{\beta'}$-L_α or $P_{\beta'}$-L_α) (also used generally in the Eqns. to indicate a non-specific transition temperature); T_p, pretransition temperature ($P_{\beta'}$-L_α); T_h, lamellar to non-lamellar phase transition temperature (L_α-H_{II} or L_α-Q_{II}).

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and phosphatidylethanolamines [2,4,9]. It is found that the theoretical fits can be improved considerably by parameter optimization on the equation for transition temperatures alone. This arises from the intrinsically better precision of the transition temperature measurements compared with the calorimetric enthalpy measurements which are otherwise required. This method possesses obvious advantages in allowing predictions of the transition temperature for systems for which calorimetric data are not available. In addition, it is found that data on the pretransition and the lamellar to nonlamellar phase transition are also amenable to the same analysis. Optimized data are also reported for other phospholipid species and for glyceroglycolipids.

A successful empirical fit to a more limited data set for the main transition of symmetrical disaturated phosphatidylcholines has previously been suggested by Nagle and Wilkinson [6]. A slightly different formulation has been offered by Mason and Huang [10,11], aimed to include also analysis of the transition temperatures of asymmetric diacyl phosphatidylcholines. A thermodynamic justification for this type of expression is given here and then tested against the thermodynamic data for a more complete set of lipid chainlengths.

Methods

For sufficiently long chainlengths, n, it might be anticipated that the transition enthalpy, ΔH_t, and the transition entropy, ΔS_t, will have essentially a linear dependence on chainlength, with constant end contributions, ΔH_0 and ΔS_0 (see, e.g., Ref. 3):

$$\Delta H_t = n \cdot \Delta H_{inc} + \Delta H_0 \tag{1}$$

$$\Delta S_t = n \cdot \Delta S_{inc} + \Delta S_0 \tag{2}$$

where ΔH_{inc} and ΔS_{inc} are the incremental values per CH_2 group. The extensive calorimetric data of Lewis et al. [2] for the gel-to-fluid transition of symmetrical disaturated phosphatidylcholines exhibit an approximately linear dependence over the range $n = 14$ to 22 * with marked deviations from linearity for $n < 14$. (Note that for chainlengths $n < 14$ the gel phase is metastable at all temperatures [2].) Linear regression over the range $n = 14$ to 22 yields values of $\Delta H_{inc} = 0.93 \pm 0.02$ kcal $\cdot$ mol^{-1} per CH_2, $\Delta H_0 = -7.1 \pm 0.3$ kcal $\cdot$ mol^{-1} ($r^2 = 0.997$), and $\Delta S_{inc} = 2.30 \pm 0.06$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1} per CH_2, $\Delta S_0 = -12.2 \pm 1.0$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1} ($r^2 = 0.996$) for the transition enthalpies and entropies, respectively.

* Where the transition enthalpy for the C22 chainlength has been corrected for the underlying pretransition (1.4 kcal/mol). Omitting this point does not affect significantly the parameters derived from the regression.

Eqns. 1 and 2 can be more conveniently written as:

$$\Delta H_t = \Delta H_{inc} \cdot (n - n_0) \tag{3}$$

$$\Delta S_t = \Delta S_{inc} \cdot (n - n'_0) \tag{4}$$

where n_0 and n'_0 are the chainlengths at which the transition enthalpy and the transition entropy, respectively, extrapolate to zero. From the linear regression data quoted above: $n_0 = 7.61 \pm 0.50$ and $n'_0 = 5.28 \pm 0.56$. It will be noted that allowing the incremental values to have a chainlength dependence of the form: $\Delta S_{inc} \approx 1/(n - d)$ in Eqns. 3 and 4, yields expressions functionally similar to those used in Ref. 11 for analyzing the chainlength dependence of the transition entropy and enthalpy for symmetrical diacylphosphatidylcholines. However, this procedure does not have the correct limiting value at infinite chainlengths and does not provide a better fit to the calorimetric data of Ref. 2 than that given by Eqns. 3 and 4.

The chainlength dependence of the transition temperature can be expressed in terms of Eqns. 3 and 4. Since the free energy change for a first order transition is zero ($\Delta G_t = \Delta H_t - T_t \cdot \Delta S_t = 0$), the transition temperature is given by [5]:

$$T_t = \Delta H_t / \Delta S_t$$

$$= (\Delta H_{inc}/\Delta S_{inc})(1 - (n_0 - n'_0)/(n - n'_0)) \tag{5}$$

This latter equation characterizes the steadily decreasing change in transition temperature with increasing chainlength. It will be noted that the functional form of Eqn. 5 is unchanged if the incremental calorimetric parameters are allowed to be chainlength dependent, provided that ΔH_{inc} and ΔS_{inc} both have the same chainlength dependence. In particular, this holds true for the form assumed in Ref. 11 and for the modification by Small [12]. Additionally, Eqn. 5 is similar to that employed in Refs. 10 and 11, although in these latter references specific values were assigned to the constants, corresponding to the chain end groups and chain asymmetry.

Results and Discussion

The data of Lewis et al. [2] for the main gel to fluid transition temperature of saturated symmetrical chain phosphatidylcholines are plotted according to Eqn. 5 in Fig. 1, where a value of $n'_0 = 5.0$ has been assumed, similar to that obtained from the calorimetric measurements. The main transition temperatures for $n = 12$ to 22 are seen to conform reasonably well to this linear behaviour in Fig. 1. Linear regression yields values of $\Delta H_{inc}/\Delta S_{inc} = 399.8 \pm 1.6$ K and $n_0 - n'_0 = 2.29 \pm 0.05$ ($r^2 = 0.997$), compared with $\Delta H_{inc}/\Delta S_{inc} = 403.4 \pm 17.4$ K and $n_0 - n'_0 = 2.33 \pm 1.06$, deduced from the calori-

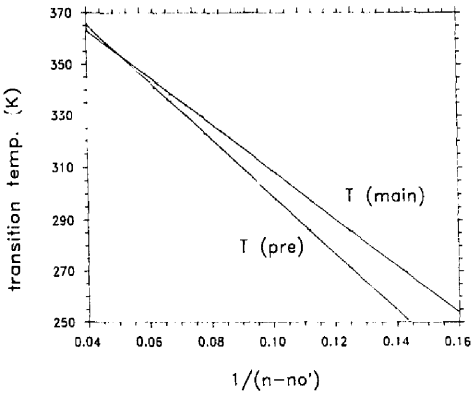

Fig. 1. Chain length dependence of the main chain melting transition temperature (○) and the pretransition temperature (△) for saturated, symmetrical straight-chain diacylphosphatidylcholines [2], plotted according to Eqn. 5. n is the number of carbon atoms in one chain, and $n'_o = 5.0$ (see text). Full lines are linear regressions.

metric data. Thus, Eqn. 5 is capable of describing the chainlength dependence of the main transition temperature reasonably well, in a manner which is consistent with the calorimetric data for the range $n = 14$ to 22.

The calorimetric data for the pretransition is not sufficiently precise to check whether it may be fitted by Eqns. 3 and 4, partly because of the difficulty in reaching true equilibrium (see Ref. 2). However, it is seen from Fig. 1 that the chainlength dependence of the pretransition temperature can be fit quite well to Eqn. 5 by using the same value of n'_o as was used for the main transition temperature. Linear regression yields values of $\Delta H_{inc}/\Delta S_{inc} = 409.7 \pm 1.8$ K and $n_o - n'_o = 2.71 \pm 0.06$ ($r^2 = 0.998$) for the pretransition over the range $n = 13$ to 21. Thus, it would appear that the chainlength dependences of the main and pretransitions are strongly related and can be explained in the same way.

Although the fits in Fig. 1 are of reasonable quality, the data for the main transition do display a slight systematic curvature. A somewhat better fit to the chainlength dependence of the transition temperature can be obtained by optimizing the parameters $\Delta H_{inc}/\Delta S_{inc}$, n'_o and $(n_o - n'_o)$ in Eqn. 5 using the simplex or non-linear least squares routines [7,13]. In this way, any errors in the calorimetric data, arising from the intrinsically lower precision of the transition enthalpy measurements compared with measurements of the transition temperature, are circumvented. This optimization yields values of $\Delta H_{inc}/\Delta S_{inc} = 421.6$ K, $n_o - n'_o = 3.45$ and $n'_o = 2.316$, corresponding to a linear regression coefficient of $r^2 = 0.999$ in a plot of the type given in Fig. 1. This value of n'_o can be compared with a value of 3 used in Ref. 6 and a value of 2.25 used in Ref. 11. The extrapolated value of the transition temperature to infinite chainlength, $T_t^{\infty} = \Delta H_{inc}/\Delta S_{inc}$, lies fairly close to the melting temperature of poly(ethylene) (414 K, see Ref. 19). However, the incremental calorimetric values are very different from those for the melting of crystalline hydrocarbons, and therefore a strict correspondence would not be expected.

A similar treatment of the pretransition temperature data for the symmetrical diacylphosphatidylcholines yields the optimized parameters: $\Delta H_{inc}/\Delta S_{inc} = 438.8$ K, $n_o - n'_o = 4.25$ and $n'_o = 1.762$, corresponding to a linear regression with $r^2 = 0.999$. A value of n'_o equal to that for the main transition has previously been used in analyzing a more limited range of pretransition temperatures [6]. The extrapolation to infinite chainlength yields a pretransition temperature that is different from that for the main transition, as might be expected from the different calorimetric parameters for the two transitions. It is predicted that the main and pretransition temperatures would coincide for a chainlength of $n = 23.6$, at a temperature of 80.3°C. Allowing for the finite transition widths, this is consistent with the main and pretransitions not being resolved in the upward scans for the C22 chainlength phosphatidylcholine [2]. It was previously estimated that the main and pretransitions would coincide at a chainlength of approx. 26, assuming that the values of n'_o were the same in both cases [6].

The above results indicate that Eqn. 5 is capable of describing the chainlength dependence of both the main transition and pretransition temperatures of saturated diacylphosphatidylcholines with a high degree of accuracy. To interpret these fits in terms of Eqns. 3 and 4 requires some revision of the chainlength dependence of the calorimetric quantities, but these lie almost within the limits of the experimental accuracy of the linearity of these values with chainlength for the longer chains (cf. above). For instance, taking only the four longer chainlengths, $n = 18$ to 21, for the calorimetric results leads to values of: $\Delta H_{inc}/\Delta S_{inc} = 428.4 \pm 29.1$ K, $n_o - n'_o = 3.79 \pm 1.57$ and $n'_o = 1.759 \pm 0.731$. As noted already, Eqn. 5 is consistent with a more general form for the chainlength dependence of the transition enthalpy and entropy than the linear dependence given by Eqns. 3 and 4. This may in part account for its success in describing the n dependence of the transition temperature over the entire range of chainlengths measured.

The data on the chainlength dependence of the main and pretransition temperatures of the ester-linked phosphatidylcholines, together with statistical information regarding the fits, are summarized in Table I. For comparison, data obtained by optimization on the main transition temperatures from a series of diacylphosphatidylcholines with methyl isobranched [14] and anteisobranched chains [15], and of diacylphosphatidylcholines with asymmetric chainlengths [21], are also included. The data for the lipids with methyl isobranched chains differ from those for the straight chain lipids, principally in that n_o and n'_o are approx. 1 unit larger. This is

as might be expected, since the branched methyl group reduces the total effective chainlength by one methylene group. The anteiso-branching has a similar effect, but also changes the incremental calorimetric values somewhat, consistent with a greater perturbing effect at this position of chain branching. The effect of the six extra methylene groups in the *sn*-2 chain of the asymmetric phosphatidylcholines is clearly seen in the reduction of n_o and n'_o by 4–5 units relative to the symmetric phosphatidylcholines. The chain asymmetry also seems somewhat to affect the incremental calorimetric values. By consideration of the chain asymmetry parameter (cf. Ref. 10), a fit to the transition temperature data for the $(n, n+6)$ PCs was made in Ref. 21 by assuming a fixed value of $n'_o = -3.5$. This yielded values of $T_t^\infty = 426.1$ K and $n_o - n'_o = 4.95$ which, although similar to those listed in Table I, give rise to a somewhat higher root mean square deviation.

The available data on the chainlength dependence of the main transition temperatures of diacylphosphatidylcholines displaying an odd-even effect [22,23], and of ether-linked phosphatidylcholines [16], are more limited, but the fitting parameters are included in Table I for a qualitative comparison. The transition temperatures of diacylphosphatidylcholines with ω-*tert*-butyl [22] and with ω-cyclohexyl [23] chains of odd or even chainlength are fitted separately. The values of n_o and n'_o for the ω-*t*-bu PCs are increased by approx. 2 units relative to the *n*-acyl PCs, corresponding to the reduction in chainlength by the dimethyl substitution, whereas for ω-cyclohexyl PCs n_o and n'_o are decreased by approx. 2 units, corresponding to the effective increase in chainlength by the cyclohexyl group that is not counted in *n*. For the dialkylphosphatidylcholines, only three data points are available. Therefore, the parameters are in principle determined exactly, but there is no check on the functional form of the chainlength dependence. The principal effect of the ether linkage is to modify somewhat the value of n'_o (and of n_o), corresponding to the different end contribution to ΔS_t (and ΔH_t).

A similar fitting procedure has been applied to the gel to fluid and to the lamellar to inverted hexagonal (H_{II}) phase transition temperatures of symmetrical saturated diacylphosphatidylethanolamines. A more limited data set for phosphatidylethanolamines was previously analyzed according to Eqn. 5, using the chainlength dependence of the calorimetric enthalpies and entropies [4]. Fits comparable in quality to those of Fig. 1 were obtained, but again the plots of the main transition temperature displayed a slight curvature. Opti-

TABLE I

Optimized parameters obtained by fits of the chainlength dependence of the transition temperatures for disaturated phosphatidylcholines and phosphatidylethanolamines, and for glucosyl diacylglycerols, according to Eqn. 5

T_t, main chain melting transition temperature. T_p, pretransition temperature. T_h, lamellar to non-lamellar (e.g., inverted hexagonal) transition temperature. rms is the root mean square value of the residuals and *N* the number of points used in the fits. Data for disaturated straight-chain phosphatidylcholines (PC) with ester-linked chains are from Ref. 2, and with ether-linked chains are from Ref. 8. Data for branched-chain phosphatidylcholines (isoacyl and anteiso) are from Refs. 14 and 15. Data for asymmetric diacylphosphatidylcholines ($(n, n+6)$ PC) with *sn*-1 chainlength *n* and *sn*-2 chainlength $n+6$ are from Ref. 21. Data for ω-tertiary-butyl (ω-*t*-bu PC) and ω-cyclohexyl (ω-cych PC) phosphatidylcholines are from Refs. 22 and 23, respectively, and are fitted separately for even and odd values of *n*. For ω-*t*-bu PC, as for isoacyl and anteisoacyl PC, *n* is the total number of C-atoms in the chain, but for ω-cych PC the cyclohexyl ring is not included in *n*. Data for disaturated straight-chain phosphatidylethanolamines (PE) with ester-linked chains are from Refs. 4, 9, 17 and 20, and with ether-linked chains are from Ref. 4. Data for branched-chain phosphatidylethanolamines (isoacyl) are from Ref. 9. Data for α- and β-D-glucopyranosyl diacylglycerols (α- and β-D-Glc-DAG) are from Refs. 24 and 25, respectively.

Lipid		$\Delta H_{inc}/\Delta S_{inc}$ (K)	$n_o - n'_o$	n'_o	rms (K), *N*
Ester PC	T_t	421.6	3.45	2.32	0.59 (11)
	T_p	438.8	4.25	1.76	0.45 (9)
Isoacyl PC	T_t	422.5	3.97	3.13	0.54 (11)
Anteiso PC	T_t	430.3	4.75	3.10	0.72 (9)
$(n, n+6)$ PC	T_t	430.4	4.51	−2.51	0.20 (9)
ω-*t*-bu PC	T_t even	407.4	4.11	4.17	0.24 (5)
	odd	401.8	4.29	2.56	0.30 (4)
ω-cych PC	T_t even	425.7	4.00	−0.43	0.33 (5)
	odd	402.9	3.10	−0.15	0.49 (5)
Ether PC	T_t	415.8	3.44	1.59	– (3)
Ester PE	T_t	424.2	2.94	1.69	0.44 (11)
	T_h	356.4	−0.188	14.198	1.64 (9)
Isoacyl PE	T_t	371.5	0.721	12.240	0.05 (4)
	T_h	349.0	−0.134	15.326	0.50 (4)
Ether PE	T_t	395.9	1.45	5.47	0.09 (4)
	T_h	322.8	−1.18	5.70	0.44 (4)
α-D-Glc-DAG	T_t	408.4	2.30	3.94	0.71 (10)
β-D-Glc-DAG	T_t	422.0	2.94	1.98	0.51 (9)

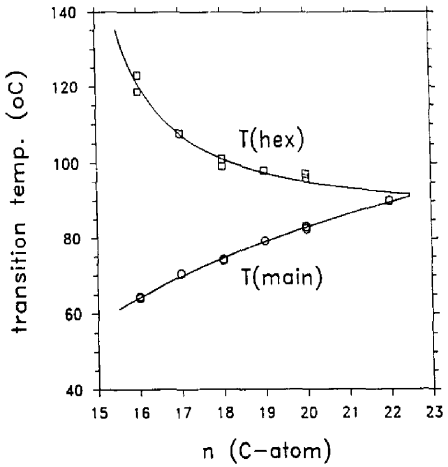

Fig. 2. Chainlength dependence of the main chain melting transition temperature (○) and the lamellar to inverted hexagonal transition temperature (□) for saturated, symmetrical, straight-chain diacylphosphatidylethanolamines [4,9,17]. n is the number of carbon atoms in one chain. Full lines are the dependences predicted by Eqn. 5, using the optimized parameters given in Table I.

mized fits to the chainlength dependence of the transition temperatures are given for a more extended data set (including concensus data for the main transition temperatures of C12 and C14 chainlengths from Ref. 20) in Fig. 2. Good fits are obtained to within the agreement of the two sets of experimental data used. The fitting parameters are given in Table I.

The main transition temperature extrapolated to infinite chainlength for the diacylphosphatidylethanolamines is comparable to that for the phosphatidylcholines. The values of n_0' and n_0 are different from those for phosphatidylcholines, however, corresponding to the different headgroup interactions (principally hydration [16]) in the two lipid classes. The sign of $n_0 - n_0'$ is opposite for the hexagonal transition to that for the main transition, corresponding to the opposite directions of the shifts with increasing chainlength in the temperatures of the two transitions. The hexagonal transition temperature extrapolated to infinite chainlength is different (lower) from that for the main transition, corresponding to the very different incremental values of the calorimetric parameters, ΔH_h and ΔS_h, for the hexagonal transition. The main and hexagonal transitions are predicted to coincide for a chainlength of $n = 22.6$ at a temperature of 91.4°C. This is close to that observed [17], and constitutes further support for the existence of transitions directly from a lamellar gel phase to an inverted hexagonal phase [18].

Data from optimizations to the chainlength dependence of the main and hexagonal transition temperatures of methyl-isobranched diacylphosphatidylethanolamines and of dialkylphosphatidylethanolamines are also given in Table I. The data correspond to four different chainlengths in each case and therefore do not constitute so exacting a test of the dependence predicted by Eqn. 5 as do the more extensive data sets considered above. However, a comparison of the parameters derived is instructive.

The parameters for the main transition of the methyl-isobranched phosphatidylethanolamines are very different from those for the straight-chain phosphatidylethanolamines or for the methyl-isobranched phosphatidylcholines. This corresponds to the much steeper chainlength dependence observed for the isobranched phosphatidylethanolamines in comparison with the main transition temperatures of the other systems. At the moment, there is no clear explanation for this. By contrast, the parameters for the hexagonal transition of the methyl-isobranched phosphatidylethanolamines are similar to those for the straight-chain phosphatidylethanolamines, except that the value of n_0' (and n_0) is one unit larger. This corresponds with the reduced effective length of the branched chains, as observed also for the main transitions of the branched-chain phosphatidylcholines.

The optimized parameters for the dialkylphosphatidylethanolamines are rather different from those for the corresponding ester-linked lipids. This may reflect the more limited number of data points available. However, the parameters do give a good description of the chainlength dependence over this range. It is predicted from the fits that the gel to fluid and hexagonal transitions will coincide for a chainlength of $n = 18.6$ at a temperature of 79.2°C. In 2.4 M NaCl, the transitions already coincide for a chainlength of $n = 18$ with a transition temperature of 80°C [4].

For comparison with the data on phospholipids, the analysis of the chainlength dependence of the main transition for two homologous series of glyceroglycolipids [24,25] is given in Table I. These data sets are also well fit by Eqn. 5. The incremental calorimetric values are similar to those for the phospholipids, and the difference in headgroups is reflected by the values of n_0 and n_0'. Significant differences are also found between the α- and β-anomers corresponding to the different orientations of the glucopyranosyl headgroup [24].

Finally, some comment is appropriate on the predictive properties of the parameters given in Table I. The root mean square values of the deviations from the experimental data points are given in the table. In general, the maximum discrepancies between predicted and measured values are of the order of one degree or less. For instance, the predicted value of T_t for didodecanoylphosphatidylcholine is -1.7°C, whereas the measured value is -2.1°C [2]. This amounts to an error in absolute temperature of 0.1%. The predicted value of T_t for diundecanoylphosphatidylethanolamine is 17.2°C,

whereas the measured value from Ref. 26 (which was not included in the fit) * is 18.6 °C, which corresponds to an error in absolute temperature of 0.5%. This somewhat larger error may arise in part from the comparison of different data sets. For instance, the predicted T_t for diheptadecanoylphosphatidylcholine is 49.6°C, and the measured value used for the fit is 49.8°C [2], whereas the experimental value reported in Ref. 10 is 49.0°C. Wherever possible, the most complete consistent data set has been used in order best to describe the chainlength dependence. This may give rise to some discrepancies with the absolute values of the transition temperatures determined in other studies which were not included in the fit.

In summary, the chainlength dependence of the temperatures of the main chain melting transition, the pretransition and the non-lamellar phase transitions can be described well by Eqn. 5, at least for the lipids tested. A thermodynamic justification can be given for this dependence, where the expression for the transition temperature is valid over a range of different chainlength dependences for the calorimetric quantities. This, together with the greater experimental precision of the measurements, makes the analysis of the transition temperature a more reliable tool than analysis of the enthalpy or entropy for investigating the chainlength dependence of the different phase transitions.

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* Including the $n = 11$ data point [26] in fitting the chainlength dependence of T_t for ester PEs yields the following parameters: $T_t^{\infty} = 428.0$ K, $n_0 - n_0' = 3.19$ and $n_0' = 1.01$, and the predicted transition temperature for $n = 11$ is then 18.2°C. In general, the omission of a single data point does not give rise to large changes in the fitted parameters. Only for the shortest chainlengths, for which T_t is changing rapidly with n, are the differences appreciable, as here.