Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

The crystallization of metal soaps and fatty acids in oil paint model systems

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List of Figures

DSC temperature programs

Pa-LO mixtures were measured on a Perkin Elmer Jade DSC with the following program: 0–100 °C with 2.5 K/min, 5 min at 100 °C, 100–0 °C with 2.5 K/min, 10 min at 0 °C, 0–100 °C with 2.5 K/min.

PbPa-LO mixtures were measured on a Netzsch STA 449 F3 Jupiter with the following program:
25–130 °C with 2.5 K/min, 5 min at 130 °C, 130–25 °C with 2.5 K/min.

ZnPa-LO mixtures were measured on a Netzsch STA 449 F3 Jupiter with the following program:
25–150 °C with 2.5 K/min, 5 min at 150 °C, 150–25 °C with 2.5 K/min.

For the measurements of phase transitions as function of heating time at 150 °C (Figure 8), samples were heated from 30 °C to 130 °C and back to 0 °C for PbPa-LO at 10 K/min using a Perkin Elmer Jade DSC. For ZnPa-LO, the maximum temperature was 150 °C, and for Pa-LO, the lower and upper temperature limits were -10 °C and 80 °C. In all cases, samples were kept at the maximum temperature for 5 minutes before the start of the cooling run.

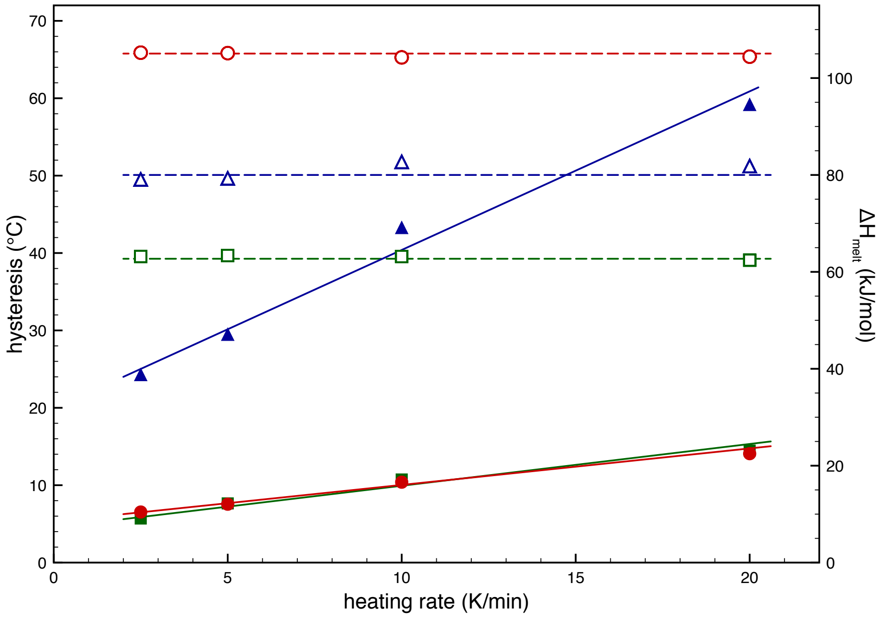

Figure S1: Hysteresis (left axis, closed symbols) and melting enthalpy (right axis, open symbols) for pure HPa (squares), PbPa (circles) and ZnPa (triangles) as a function of heating rate. Similar results were found for mixtures of HPa, PbPa and ZnPa in linseed oil.

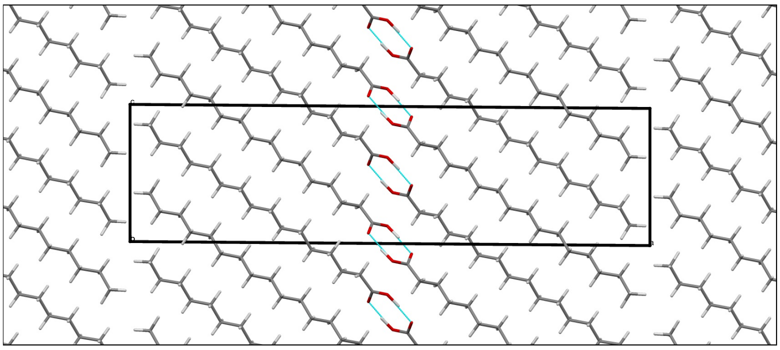

Figure S2: View along the *b*-axis in the crystal structure of palmitic acid in the C form [Moreno, E., Cordobilla, R., Calvet, T., Lahoz, F. J., and Balana, A. I. (2006). *Acta Crystallographica*, C62, 129–131]. The black box indicates the unit cell and hydrogen bonds are indicated as dashed blue lines. Note that the structure consists of stacked palmitic acid 'dimers', bound by hydrogen bonds between the carboxylic acid headgroups.

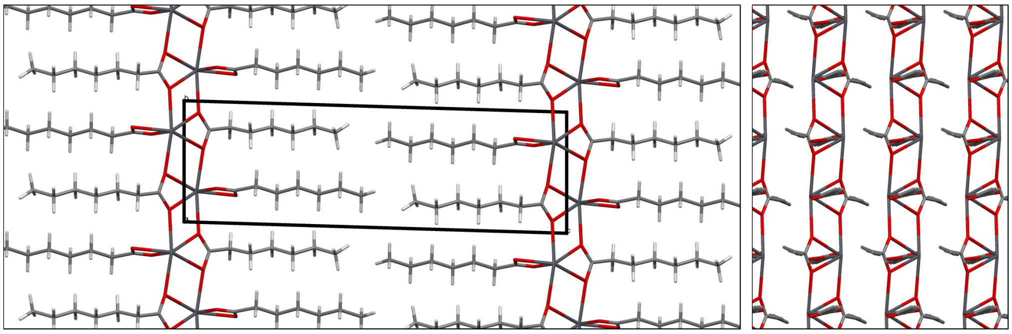

Figure S3: (*left*) View along the *a*-axis in the crystal structure of lead heptanoate and (*right*) a view along the diagonal of the *c*-axis (hydrogens are omitted for clarity) [Lacouture, F., François, M., Didierjean, C., Rivera, J.-P., Rocca, E., and Steinmetz, J. (2001). *Acta Crystallographica*, C57, 530–531]. The black box indicates the unit cell, and lead atoms are shown in dark grey. Note that the structure is effectively a 1D-coordination polymer, consisting of bidentate $Pb(C_6H_{13}COO)_2$ units joined together in a linear fashion by Pb−OCO−Pb bonds. The crystal structure of PbPa is thought to be analogous to that of lead heptanoate, given the linearity of the *d*-spacings in the homologous series of lead alkanoates [Martínez Casado, F. J., García Pérez, M. V., Redondo Yélamos, M. I., Rodríguez Cheda, J. A., Sánchez Arenas, A., López-Andrés, S., . . . Santamaría, J. (2007). *Journal of Physical Chemistry C*, 111, 6826–6831].

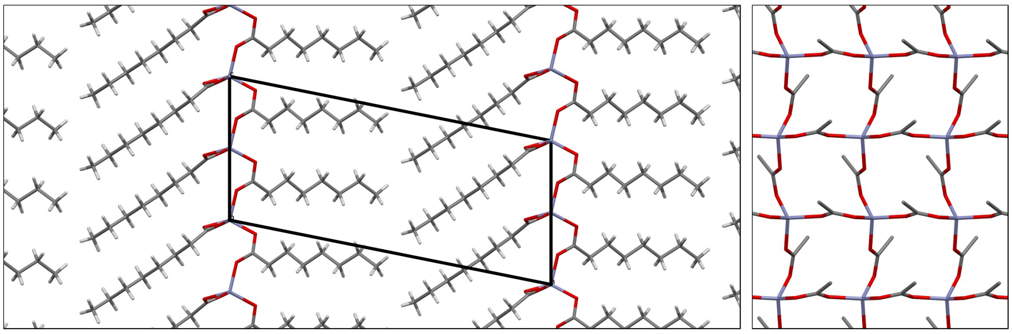

Figure S4: (*left*) View along the *b*-axis in the crystal structure of zinc octanoate and (*right*) a view along the diagonal of the *ac*-plane (hydrogens are omitted and only C1 and C2 atoms are shown for clarity) [Lacouture, F., Peultier, J., François, M., and Steinmetz, J. (2000). *Acta Crystallographica*, C56, 556–557]. The black box indicates the unit cell, and zinc atoms are shown in purple. Note that the structure is effectively a 2D-coordination polymer, with a *bc*-plane that contains covalent Zn−OCO−Zn bonds. Because each zinc atom is surrounded by oxygen atoms from four different carboxylate groups in monodentate coordination, the structure is not easily broken up in $Zn(C_7H_{15}COO)_2$ units, and therefore a significant change in the coordination structure probably occurs upon melting. The crystal structure of ZnPa is thought to be analogous to that of zinc octanoate, given the linearity of the *d*-spacings in the homologous series of zinc alkanoates [Hermans, J. J., Keune, K., van Loon, A., Corkery, R. W., and Iedema, P. D. (2014). *Polyhedron*, 81, 335–340].

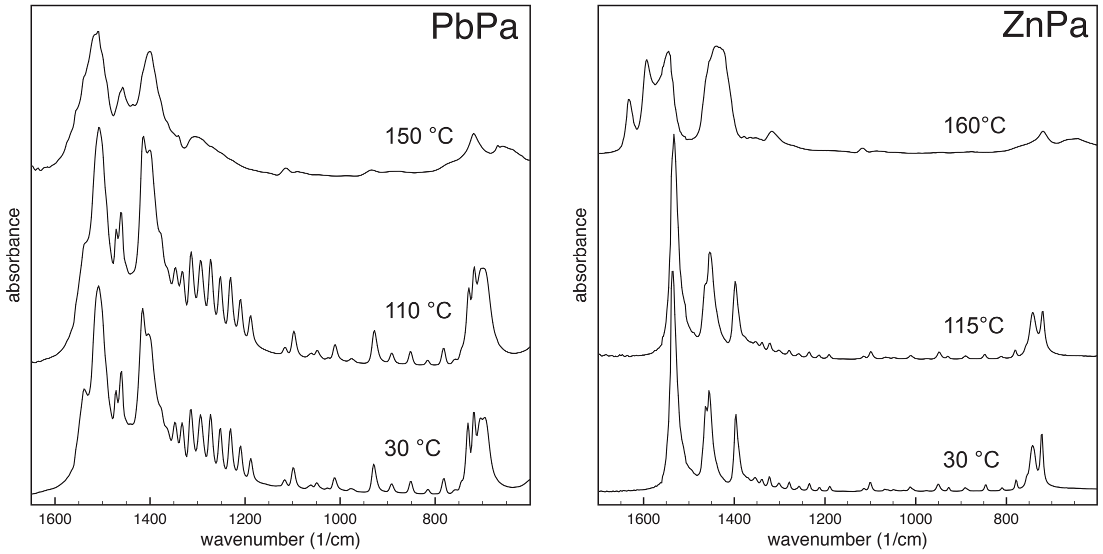

Figure S5: ATR-FTIR spectra of PbPa and ZnPa at 30 °C, just before melting and in the melt. Both metal soaps show a loss of CH_2 progression bands in the 1200-1 400 cm^{-1} region and a loss of fine structure in the CH_2 band around 1 460 cm^{-1}. In PbPa, the ν_a COO^- band merely broadens upon melting, while in ZnPa the single ν_a COO^- band splits into three new well-defined bands, indicating a significant change in coordination environment.