



III International Scientific Conference on “Sustainable and Efficient Use of Energy, Water and Natural Resources”

PHYSICOCHEMICAL PROPERTIES OF N-ALKANE NANOSIZED DISPERSIONS

Vladimir Kuryakov

vladimir.kuryakov@gmail.com

Oil and Gas Research Institute of Russian Academy of Sciences
Moscow, Russia



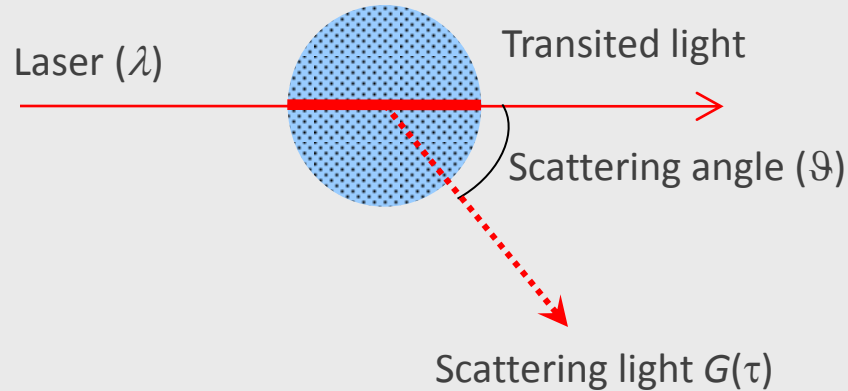
Principle of the DLS method

The DLS method consists in analyzing the velocity distribution of particles movement by measuring dynamic fluctuations of light scattering intensity:

- The disperse particles or macromolecules suspended in a liquid medium undergo **Brownian motion** which causes fluctuations of local concentration of the particles, resulting in local inhomogeneities of the refractive index. This in turn results in fluctuations of intensity of the scattered light.
- The **diffusion coefficient** of the particles is inversely proportional to the decay time of light scattering fluctuations. The decay time is obtained from the time-dependent correlation function of the scattered light.
- The **particle size** is calculated in accordance with Stokes-Einstein formula relating the particle size to the diffusion coefficient and viscosity.

Principle of the DLS method

Dynamic Light Scattering



Correlation function

$$G(\tau) = \langle I(t) \cdot I(t - \tau) \rangle = \lim_{t_m \rightarrow \infty} \frac{1}{t_m} \int_0^{t_m} I(t) \cdot I(t - \tau) dt$$

$$G(\tau) = a \cdot \exp(-2\tau/\tau_c) + b$$

Diffusion equation

$$\partial c(\vec{r}, t) / \partial t = D \Delta c(\vec{r}, t)$$

Solution of diffusion equation

$$1/\tau_c = Dq^2$$

Wave vector of scattered light

$$q = (4\pi n / \lambda) \sin \theta / 2$$

STOKES-EINSTEIN EQUATION

$$R_h = \frac{k_b T}{6\pi\eta D}$$

Photocor Instruments

Features (Photocor Complex)

- Full-featured multi-angle dynamic and static light scattering, fast measurements, real-time size monitoring of nanoparticles
- Modular architecture, rigid design, no optical table needed, easily configurable by user
- Easy-to-prepare samples, suitable for various commercial sample cells and vials, replaceable index-matching vat system
- Stepper-motor controlled turntable, compatibility with various APD photon counting systems
- Unique flex-logic single-board correlator, linear and multiple-tau time scale, upgrade of hardware configurations
- Original light-scattering geometry for particle sizing of opaque dispersions
- Exceptional quality and reliability with all light scattering features for optimal price
- Particle size measurements in opaque dispersions are available in back-scattering mode.
- For Photocor Compact-Z: zeta potential measurements

Measurement range	Particle size: 0.5 nm to 10 μm ¹ (diameter) Diffusion coefficient: 10 ⁻⁵ ... 10 ⁻¹⁰ cm ² /s Molecular weight: 10 ³ ... 10 ¹² g/mol
Accuracy	±1%
Sample volume	50 μL to 10 mL
Scattering angle	10° ... 150°, accuracy 0.01°, stepper-motor controlled turntable
Signal processing	Auto- and cross-correlation operation modes. Linear and logarithmic (multiple-tau) time scale. True real-time operation up to the fastest sample-time of 10 ns
Laser	TEC stabilized diode laser 638 nm, 25 mW ³
Thermostat	Temperature range: 5°C - 100°C (thermoelectric module), accuracy 0.1°C
Dimensions / weight / power	420 x 230 x 200 mm / 14 kg / 100...220 V, 85 W



Photocor Complex
(price from 48300 euro)



Photocor Compact-Z
(price from 31100 euro)



Photocor Mini
(12150 euro)

Photocor Instruments

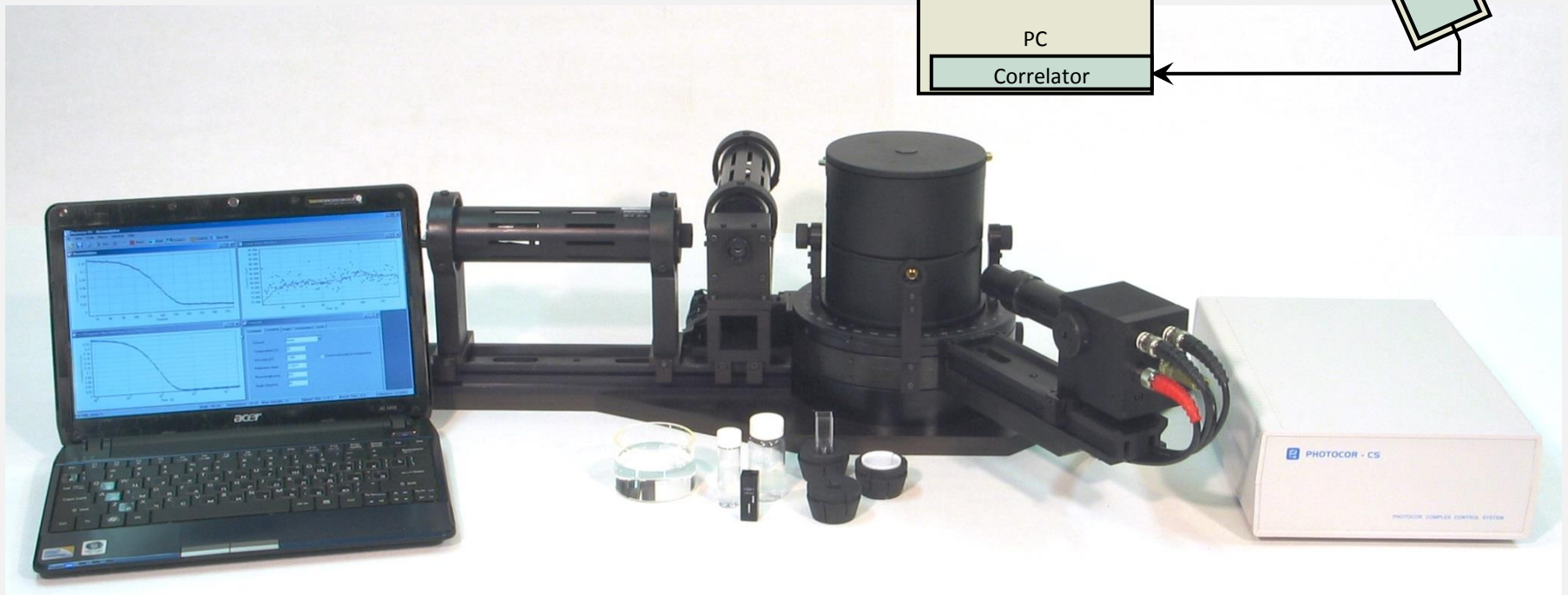
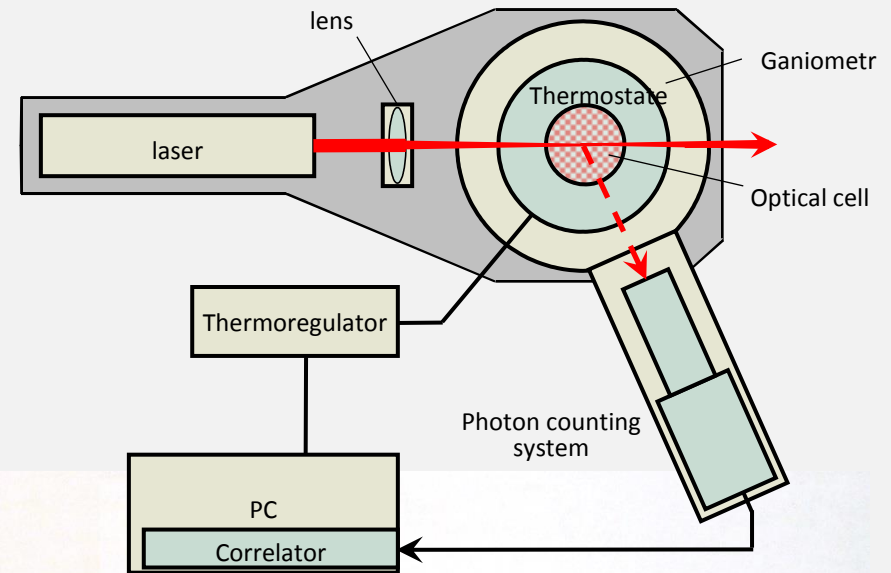
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e-mail: info@photocor.com
website: www.photocor.com

Photocor Ltd.

Moscow, Russia, 5, 2nd Entuziastov st, bldg 40, office 24, 111024,
e-mail: info@photocor.ru
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Photocor Complex (device photo and block diagram)

Measurement of nanoparticle size, diffusion coefficient, molecular weight of polymers in solutions



Emulsions

Emulsion is a mixture of two or more liquids that are normally immiscible. In an emulsion, one liquid (the dispersed phase) is dispersed in the other liquid (the continuous phase). The diameters of the droplets constituting the dispersed phase usually range from approximately 10 nm to 100 μm . The three basic types of emulsions are: direct (oil dispersed in water, o/w), reversed (water dispersed in oil, w/o) and bicontinuous.

Microemulsions are clear, thermodynamically stable, isotropic liquid mixtures of oil, water and surfactant. In contrast to ordinary emulsions, microemulsions form during simple mixing of the components and do not require the high shear conditions. Diameter of microemulsion is within approximately from 10 to 100 nm.

Nanoemulsions — require specialized equipment to be produced. Nanoemulsions are kinetically stable. Diameter of nanoemulsion is within approximately from 20 to 500 nm.

APPLICATIONS

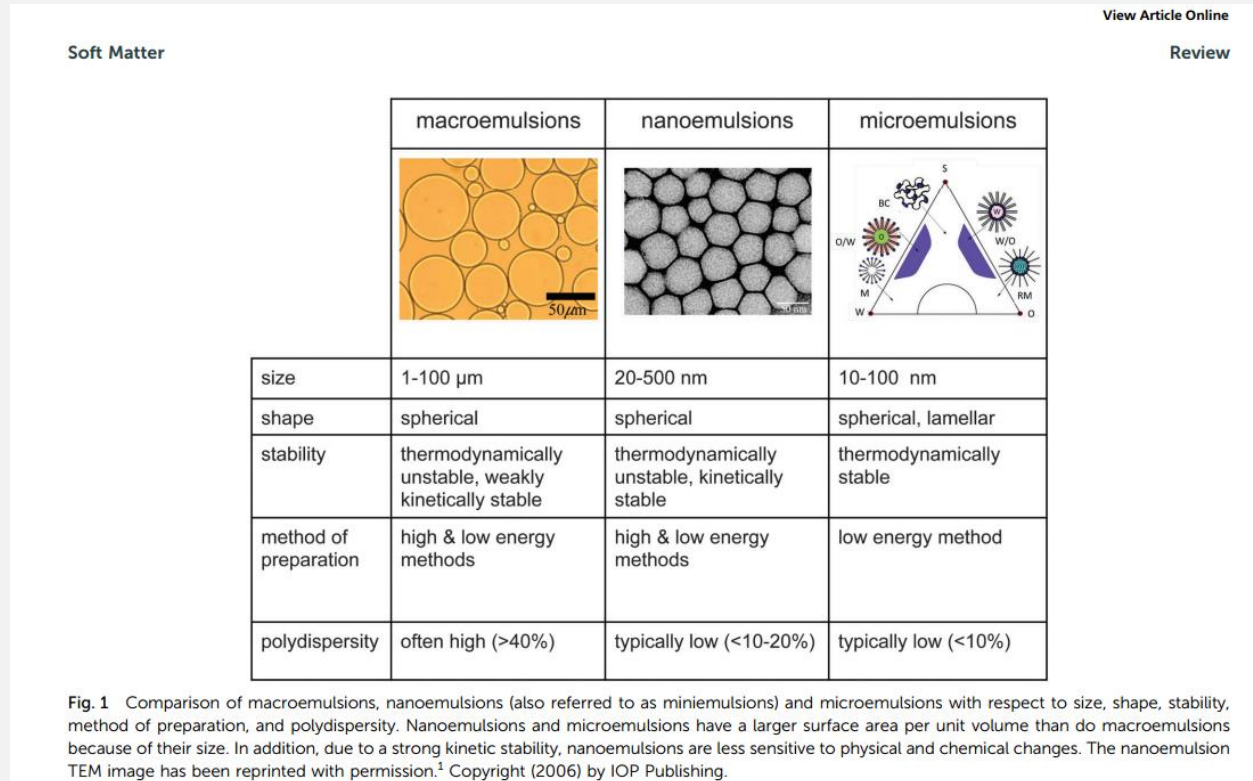
In food (mayonnaise, milk, butter); Health care (cosmetics, creams, drug deliver); Chemical synthesis (Emulsions are used to manufacture polymer dispersions – polymer production in an emulsion 'phase') and many other...

Paraffin emulsions – Phase Change Slurry (PCS) (PCS can store or transfer amounts of thermal energy by using both the sensible heat capacity of the carrier fluid and PCM as well as the latent heat capacity of the PCM.), Hydrophobization, Transport.

Types of emulsions

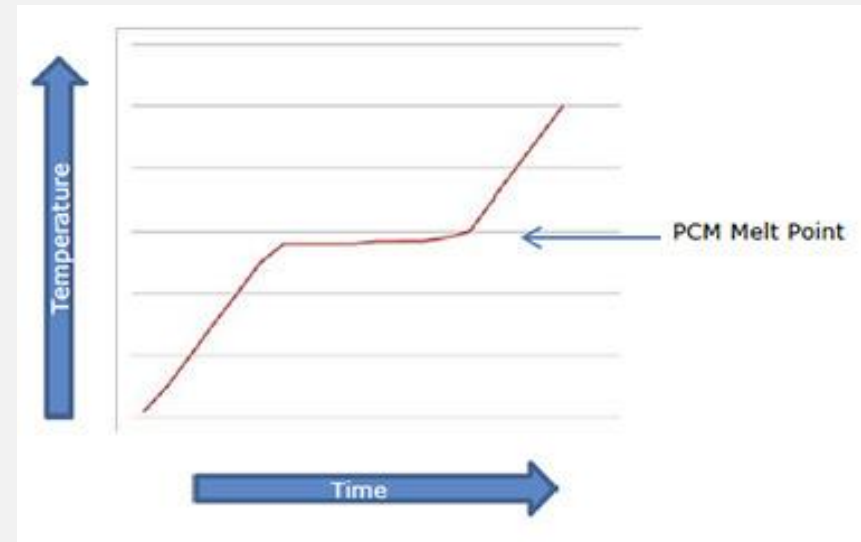
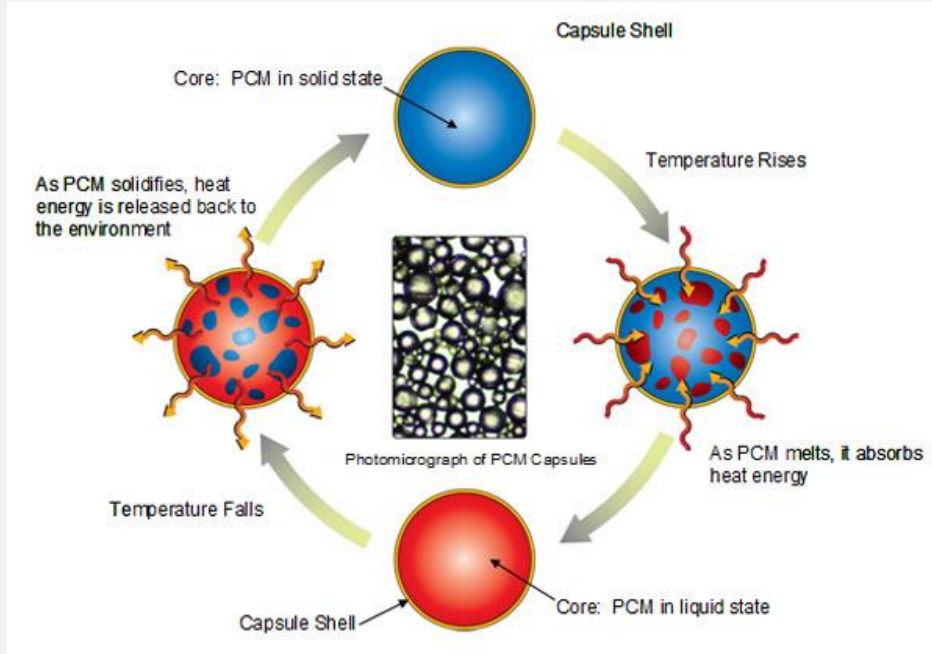
Emulsion is a mixture of two or more liquids that are normally immiscible. In an emulsion, one liquid is dispersed in the other liquid (dispersed phase and continuous phase).

The three basic types of emulsions are: direct (oil dispersed in water, o/w), reversed (water dispersed in oil, w/o) and bicontinuous.



Application of paraffin emulsions – Phase Change Slurry (PCS), Hydrophobization

How do PCM work?



Certain amount of heat, the so-called latent heat, is absorbed or released when a material melts or solidifies, respectively.

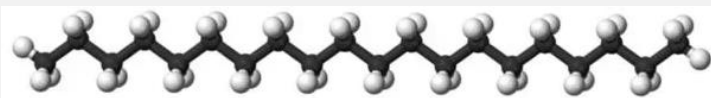
The enthalpy varies depending on the PCM material itself. In the case of PCMs, the enthalpy is typically measured in Joules/gram. The higher the number of Joules per gram, the longer the PCM will provide a cooling effect.

PCM application

- Microencapsulated phase change materials. microteklabs.com
- Knauf Comfortboard Phase change plasterboard (PCM from BASF) this innovative plasterboard absorbs heat energy during the day and releases it at night, keeping living and work areas at a steadier temperature.
- NASA's Game Changing Development is taking on a technology development and demonstration effort to design, build, and test the next generation of Phase Change Material Heat Exchangers (PCM HXs) on the International Space Station.
<https://www.youtube.com/watch?v=BG2w4wb4Q5w>

Years	
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Rotator phases of the normal alkanes



General chemical formula of *n*-alkanes C_nH_{2n+2}

Alkanes exhibit two unique features:

Between the fully ordered crystalline phases of the *n*-alkanes and the isotropic liquid phase, occurs a series of phases known as rotator phases, which are layered and are typically crystals with long range positional order of the molecules in three dimensions. But there is a rotational degree of freedom of the molecule about its long axis.

RI phase has molecules untilted with respect to the crystalline layers and contains a rectangularly distorted hexagonal lattice and a bilayer stacking sequence [also referred to as face centered orthorhombic (FCO)].

RII phase has molecules untilted with respect to the layers which are packed in a hexagonal lattice with a trilayer stacking sequence [also referred to as rhombohedral (RR)].

RIII phase is tilted and triclinic.

RIV phase is tilted and monoclinic.

RV phase is similar to RI but with the molecules tilted.

In shorter chain lengths the general phase sequence was reported to be liquid-->RII-->RI-->crystal and in chains C_{27} and longer: liquid-->RIV-->RIII+crystal.

Kuryakov V.N. OGRI RAS

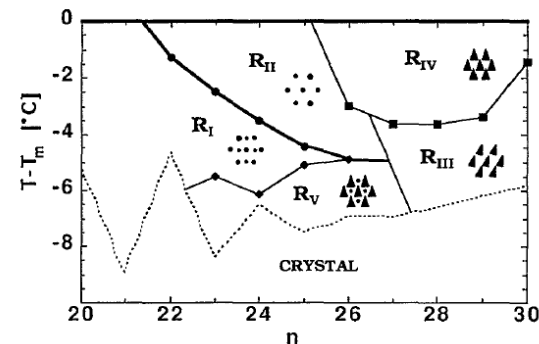


FIG. 2. Chain length-temperature phase diagram plotted with respect to the melting temperature (T_m). Measurements were performed only on pure materials so the lines passing through nonintegral n are merely guides to the eye and suggest what might occur in mixtures or if chain length could be treated as a continuous variable. The dashed line follows the rotator-crystal transition on cooling.

E. B. Sirota, D. M. Singer. J. Chem. Phys. 101, 10873 (1994);
Jung, Yun, and Jeon. J. Chem. Phys. 136, 104903 (2012)

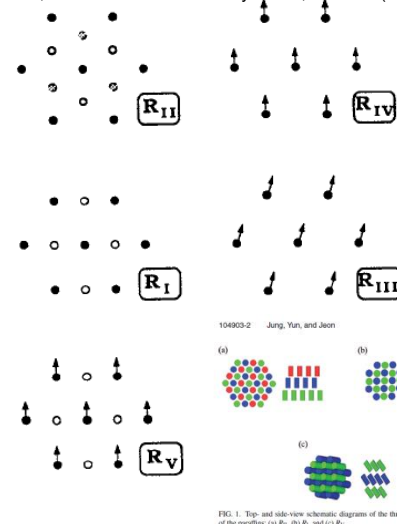


FIG. 1. Top- and side-view schematic diagrams of the three rotator phases of the paraffins: (a) R_{II} , (b) R_{III} , and (c) R_{IV} .

FIG. 3. Schematic showing the symmetries of the five rotator phases. The unfilled circles represent the chain end positions in the second layer of a bilayer structure. The gray circles for the R_{III} phase represent the third layer in a trilayer structure. The arrows represent the tilt direction in the tilted structures.

Surface freezing in Alkanes

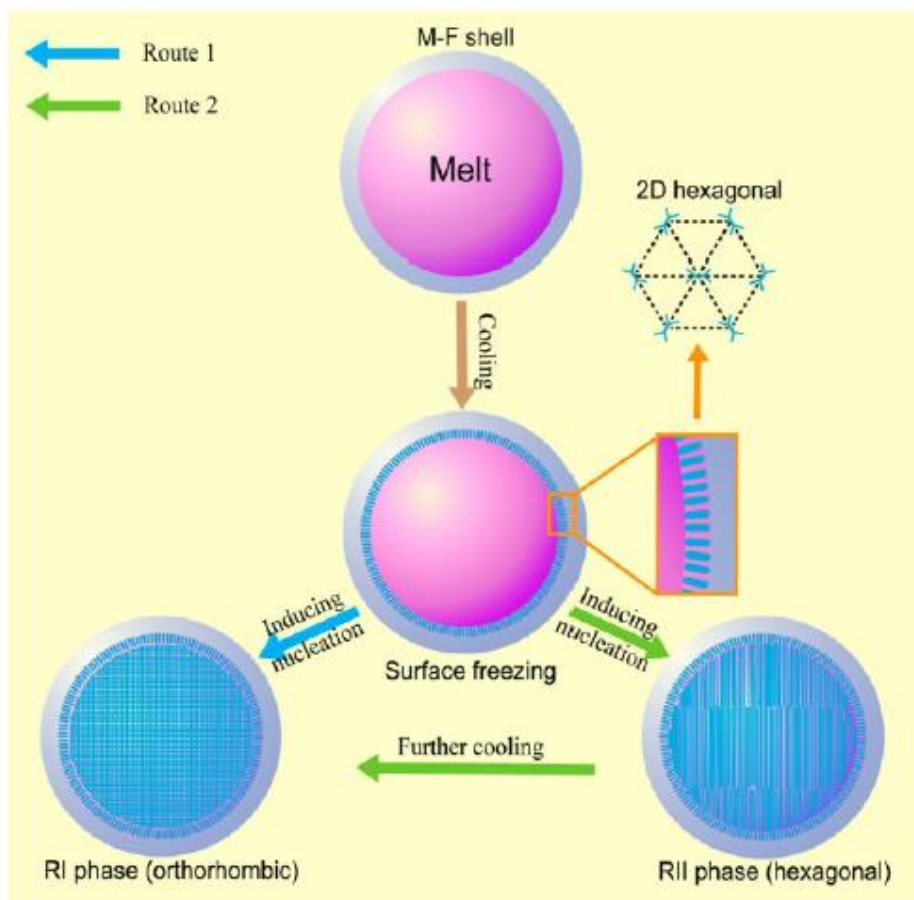


FIGURE 9. Schematic illustration of surface freezing effect on bulk crystallization.

Crystallization of Normal Alkanes in Confined Geometry Su et al. ACCOUNTS OF CHEMICAL RESEARCH A, 2013

The unique feature of n-alkane ($15 < n < 50$) is the surface freezing effect. In general, the entropy of molecules at the surface of a crystal is higher than that in the bulk. Hence, surface melting occurs in virtually all materials studied to date, i.e., the surface melts at a lower temperature than the bulk. In alkanes, however, the opposite effect, i.e., surface freezing. **A crystalline monolayer is formed at the surface of the molten alkane at a temperature of up to ~ 3 °C above the bulk freezing temperature, and persists down to bulk freezing.**

DCS and XRD

Xie et al.

Widely used methods for studying phase transitions of paraffins are calorimetry and X-ray diffraction methods.

In this work, we propose a new approach for determination the temperatures of phase transitions of *n*-alkanes, based on the optical methods. An approach similar to droplet technique (D. Turnbull and R. L. Cormia. Kinetics of crystal nucleation in some normal alkane liquids. J. of Chem.Phys. 1961.)

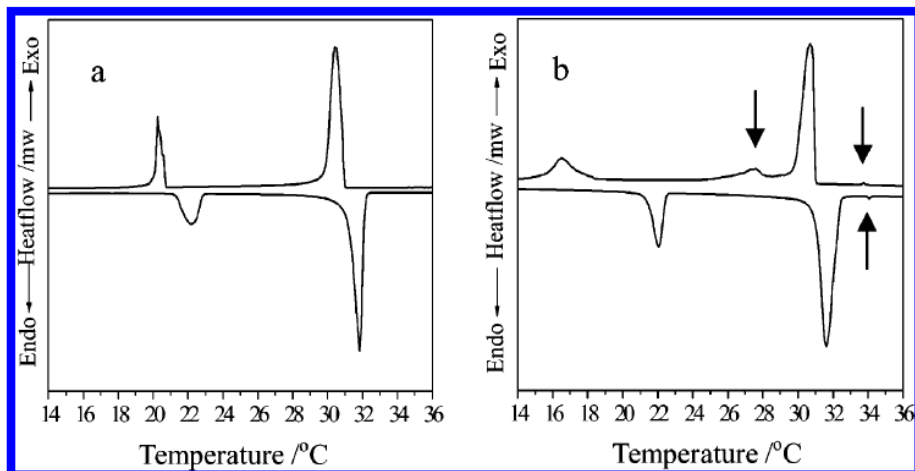


Figure 2. DSC traces of *n*-nonadecane during the heating and cooling processes: (a) pure *n*-nonadecane; (b) microencapsulated *n*-nonadecane.

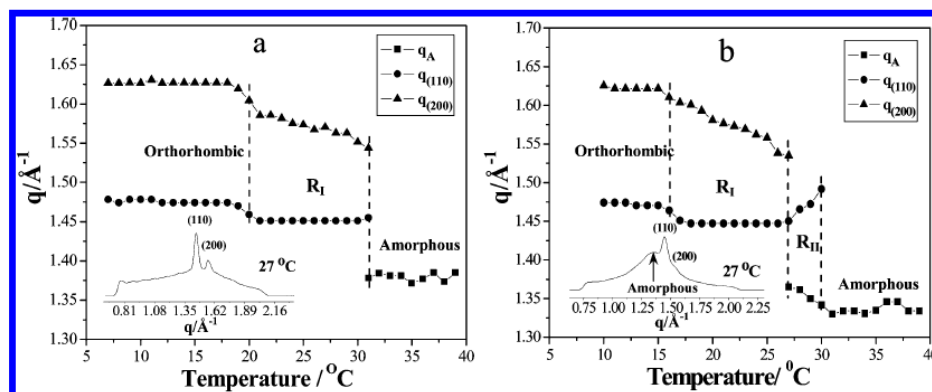
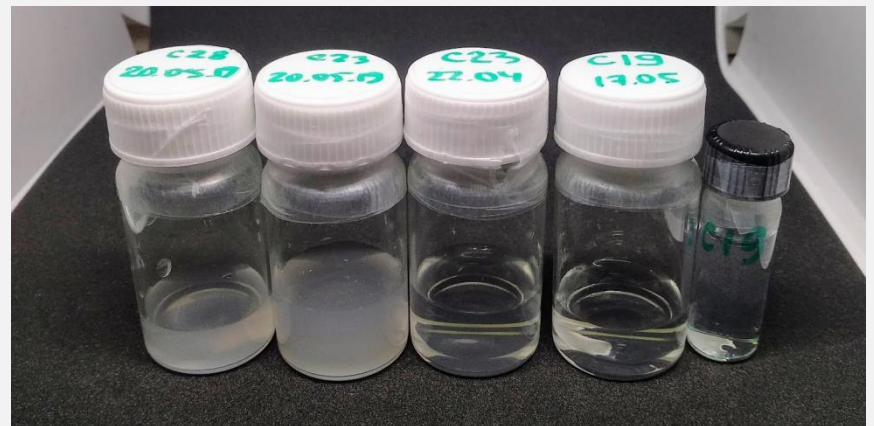


Figure 4. The peak positions of the amorphous state (square) and 110 (rhombohedron) and 200 (triangle) crystal faces as a function of temperature for both (a) pure *n*-nonadecane and (b) microencapsulated *n*-nonadecane. The cooling rate was 0.5 °C/min. The interval between the data acquisition was 3 min.

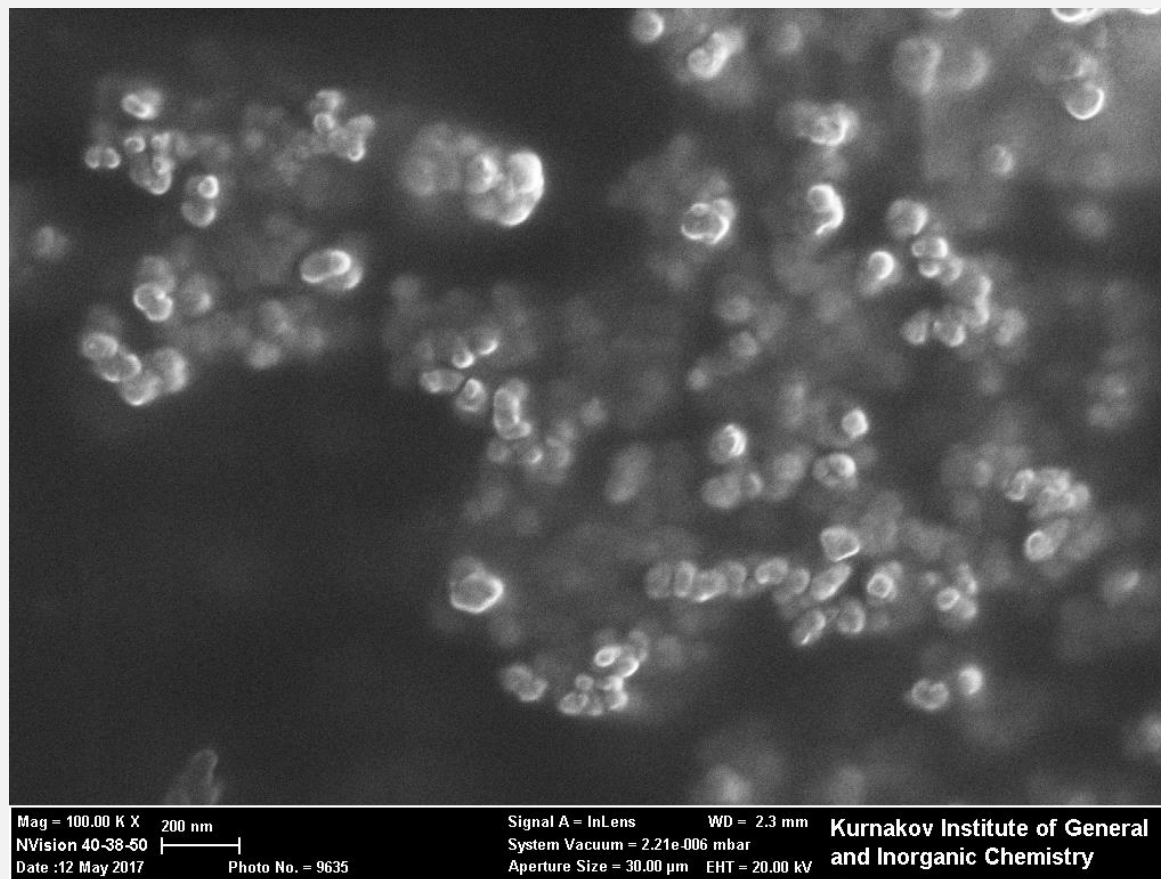
Sample preparation and measurement procedure

For the preparation of emulsions, pure n-alkanes $C_{19}H_{40}$ to $C_{28}H_{58}$ (ACROS ORGANICS, purity > 98 - 99%) and bidistilled water were used (0.01 % weight n-alkane in water). Dispersing of the n-alkane - water mixture was carried out at a temperature above the melting point of the n-alkane used (Ultrasonic disperser UZDN-A 22 kHz, 75 W, dispersing time about 30 seconds).

- Measured by the DLS the hydrodynamic radius was in the range from 90 to 120 nm. After filtering through 0.1 μm filter there are still particles in the samples (~ 35 nm)
- Zeta-potential about -30 mV
- All measurements were made at an angle of 90 degree
- The original samples were diluted 100 times with distilled water for DLS and LS measurements
- The temperature step 0.1 $^{\circ}\text{C}$, constant rate of heating and cooling about 2 $^{\circ}\text{C}$ per hour

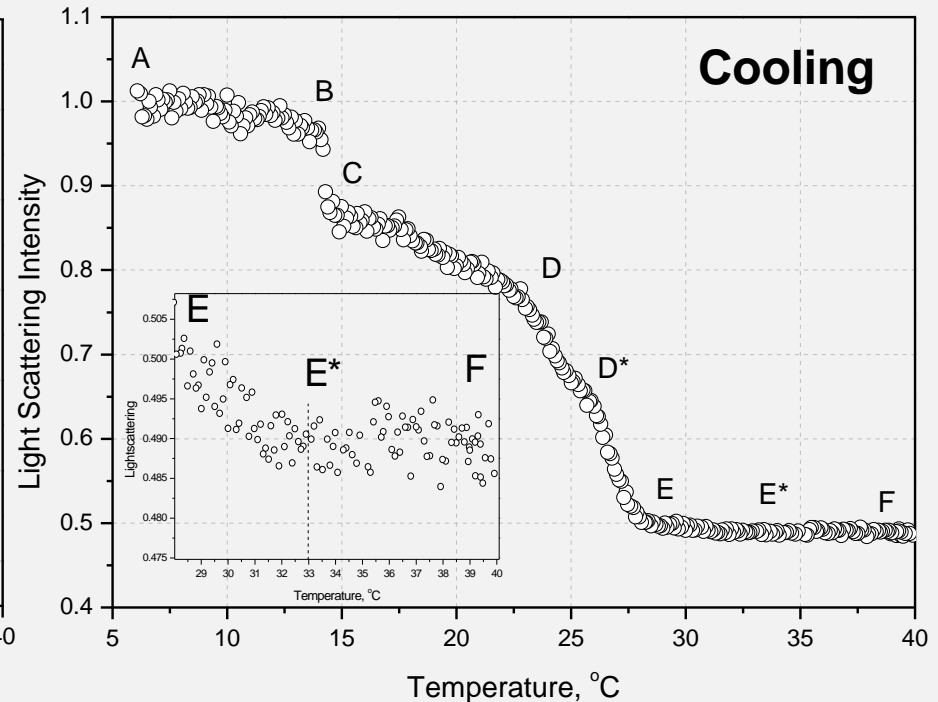
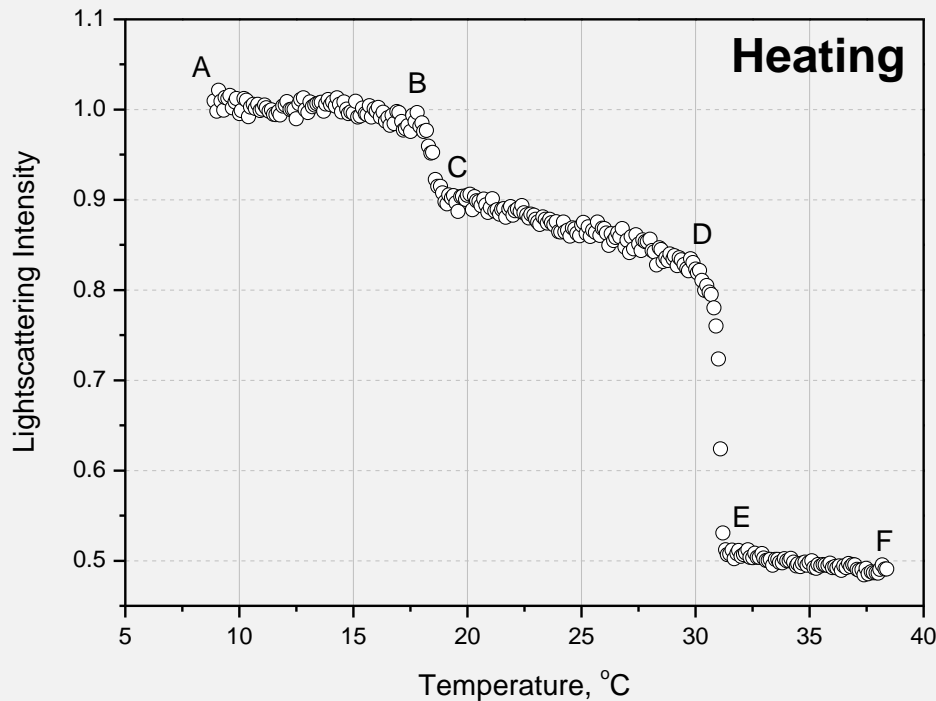


SEM



Dried sample $C_{28}H_{58}$

$C_{19}H_{40}$ Nonadecane

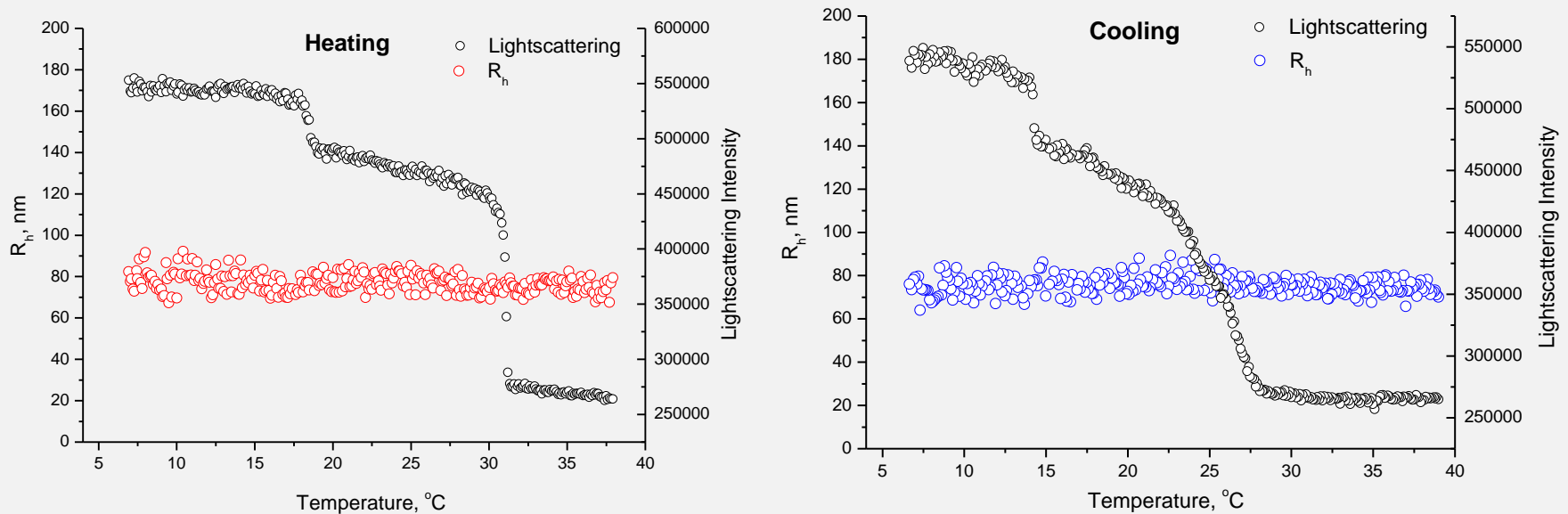


Light scattering temperature dependence for Nonadecane nanoemulsion

For heating: A-B region is crystal phase of Nonadecane, B-C is crystal-crystal phase transition from ordered solid (orthorhombic) to disordered solid rotator phase RI which is distorted-hexagonal lattice. C-D region is a region of RI phase of Nonadecane, D-E is the phase transition RI to liquid state i.e. melting and E-F region is a region there a Nonadecane is an isotropic liquid.

For cooling: F-E is liquid state of Nonadecane with, as we assume, E*-E surface freezing region of paraffin in emulsion.

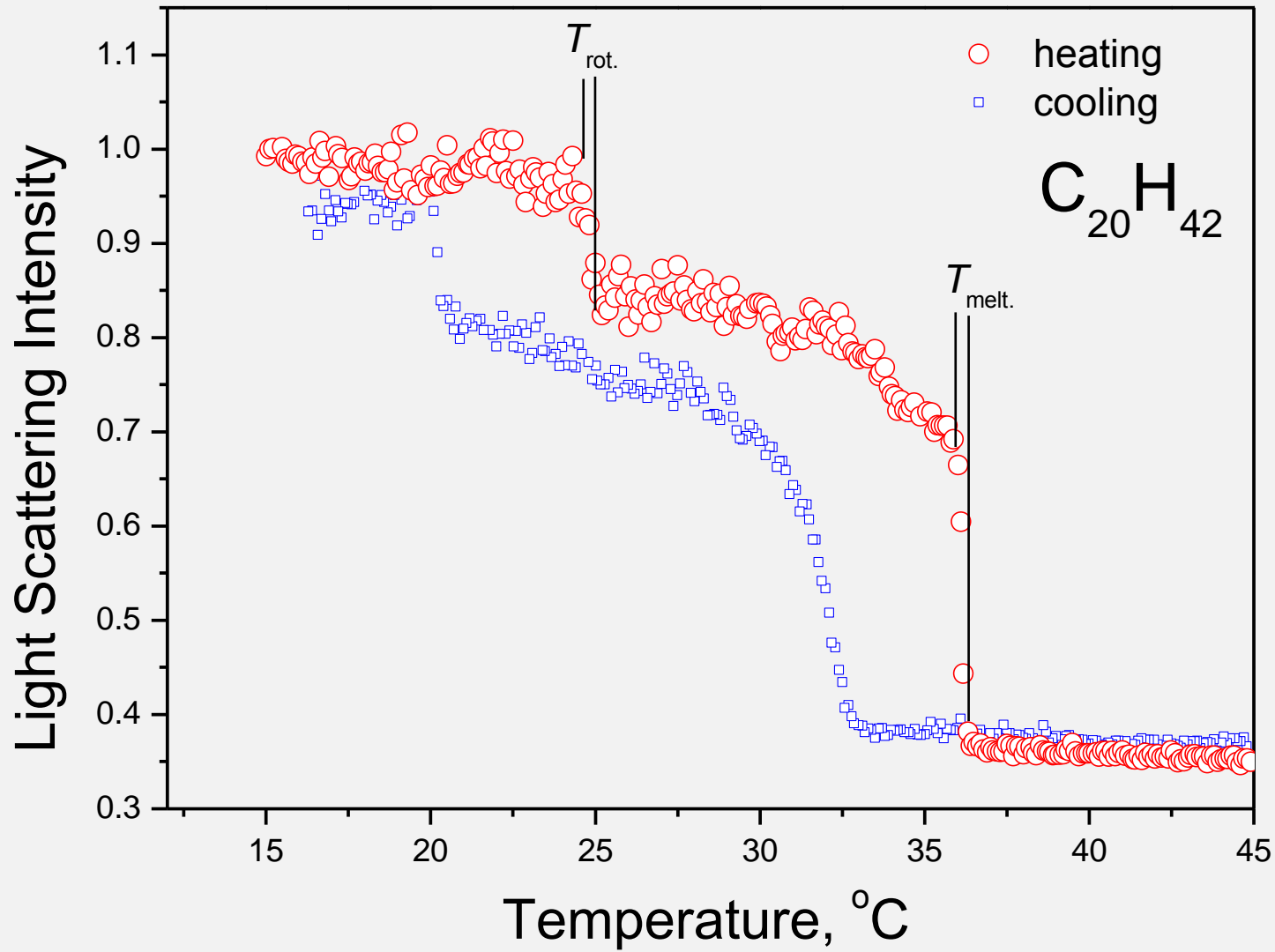
$C_{19}H_{40}$ Nonadecane



R_h and light scattering temperature dependence for Nonadecane
This sample has been pre-filtered through 0.2 μm filter

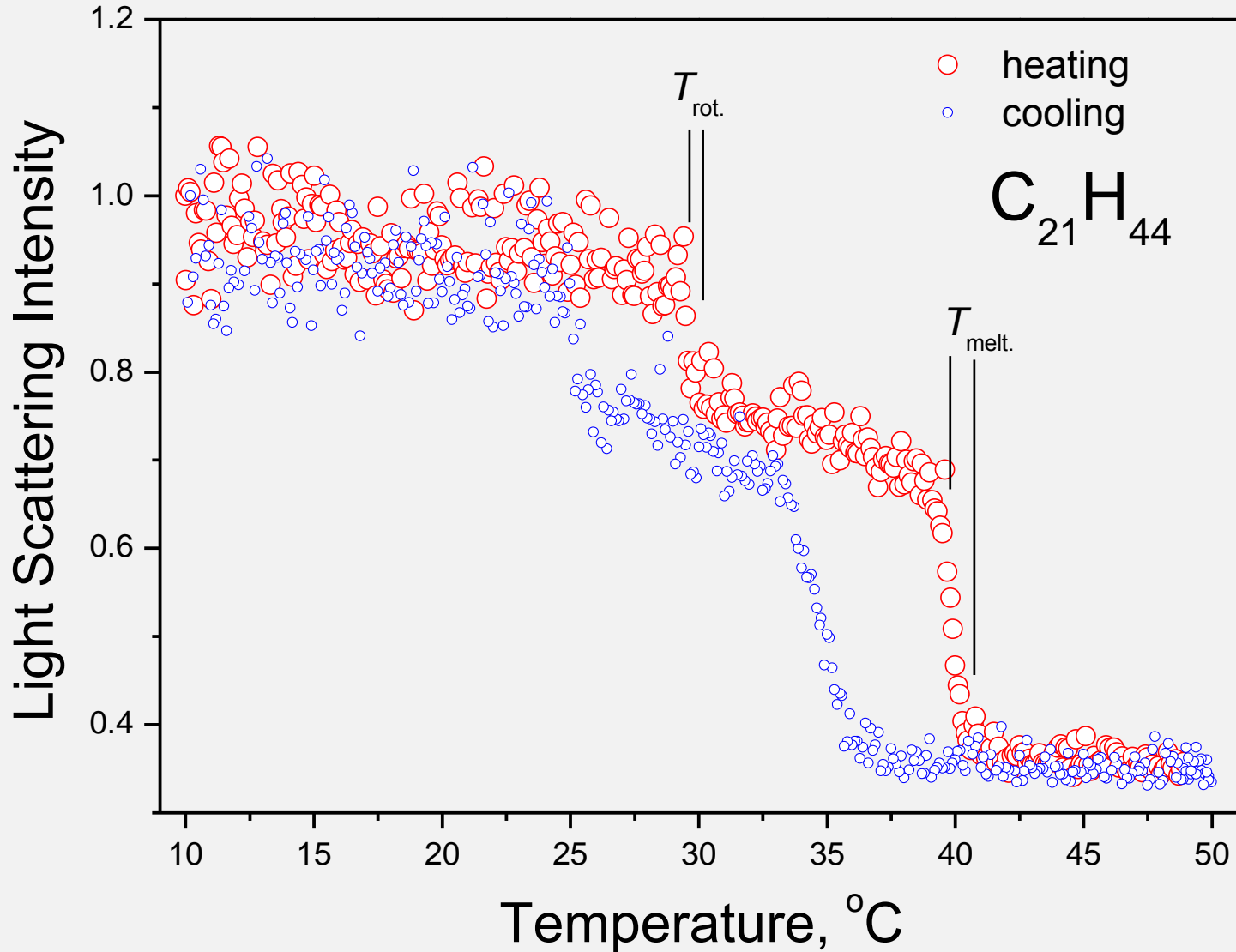
The intensity of light scattering from samples of paraffin nanoemulsion will change when one of the following change: concentration, size, the shape of paraffin particles or refractive index ratio of paraffin particles and water.

$C_{20}H_{42}$ Icosane



Light scattering temperature dependence for Icosane

$C_{21}H_{44}$ Heneicosane



Light scattering temperature dependence for Heneicosane

$C_{23}H_{48}$ Tricosane

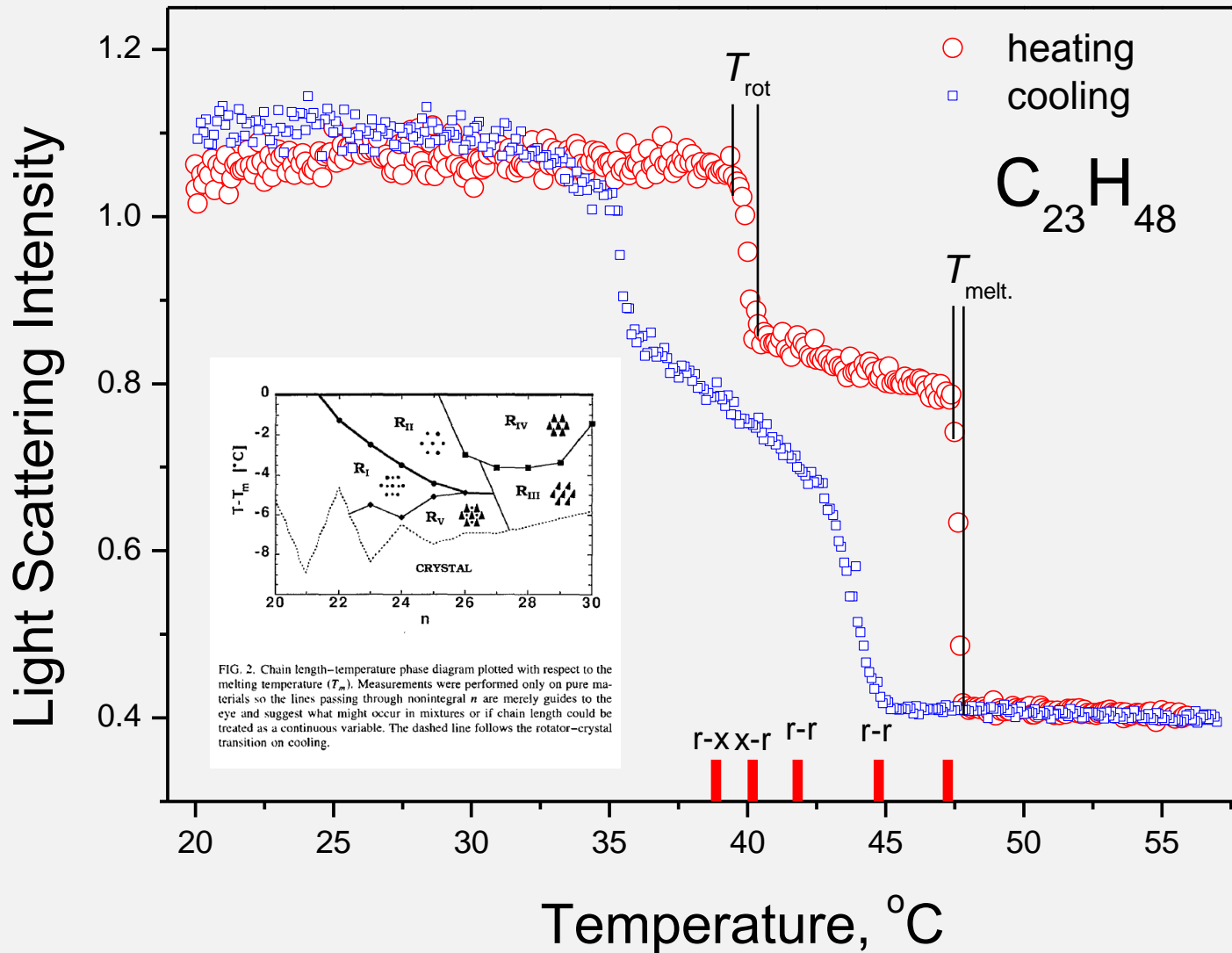
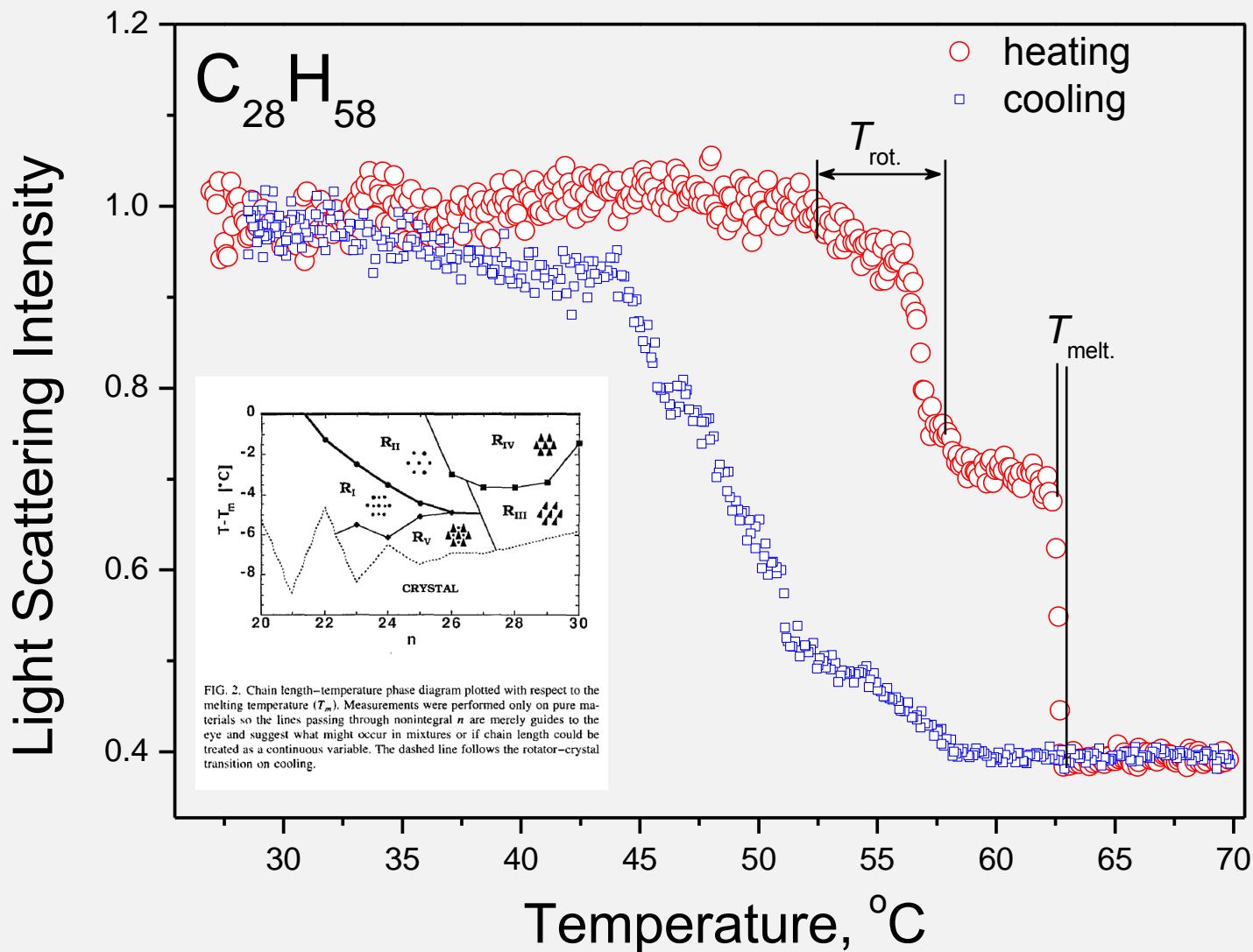


FIG. 2. Chain length-temperature phase diagram plotted with respect to the melting temperature (T_m). Measurements were performed only on pure materials so the lines passing through nonintegral n are merely guides to the eye and suggest what might occur in mixtures or if chain length could be treated as a continuous variable. The dashed line follows the rotator-crystal transition on cooling.

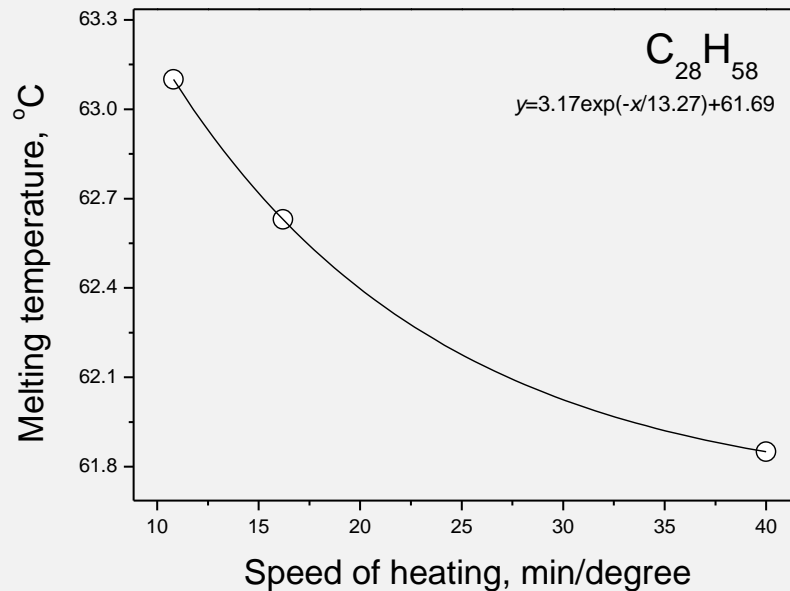
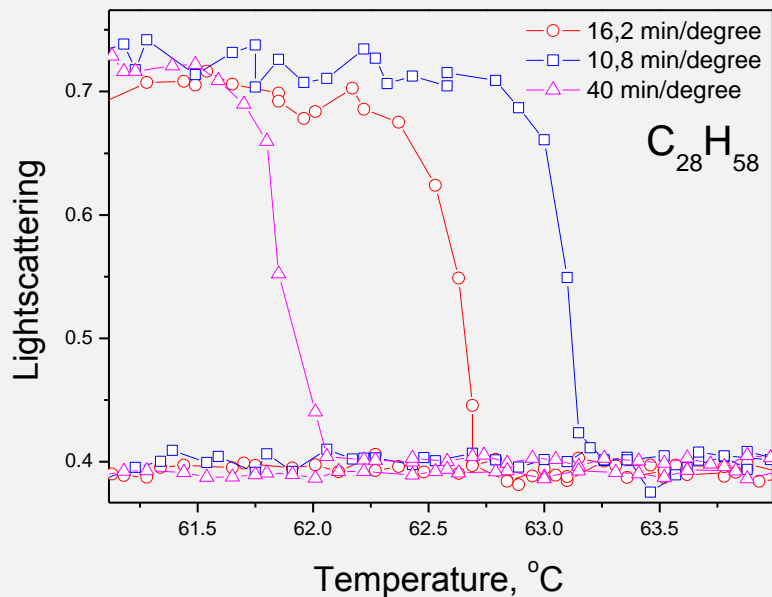
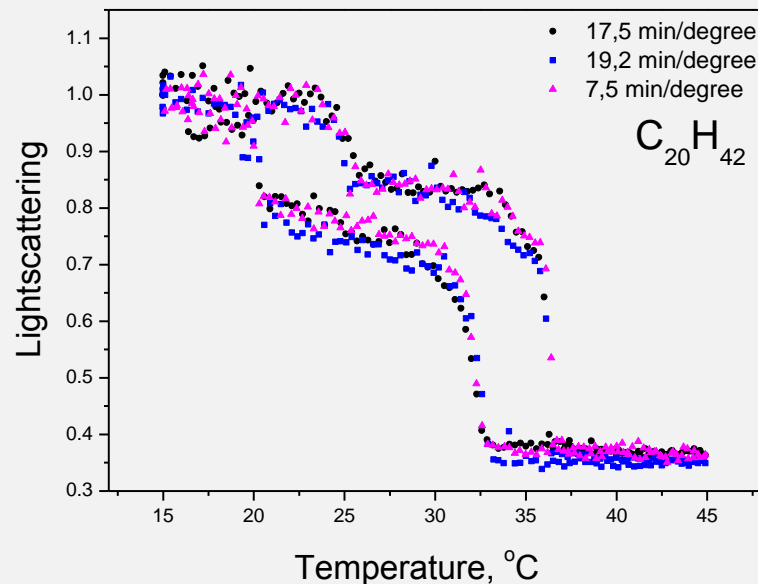
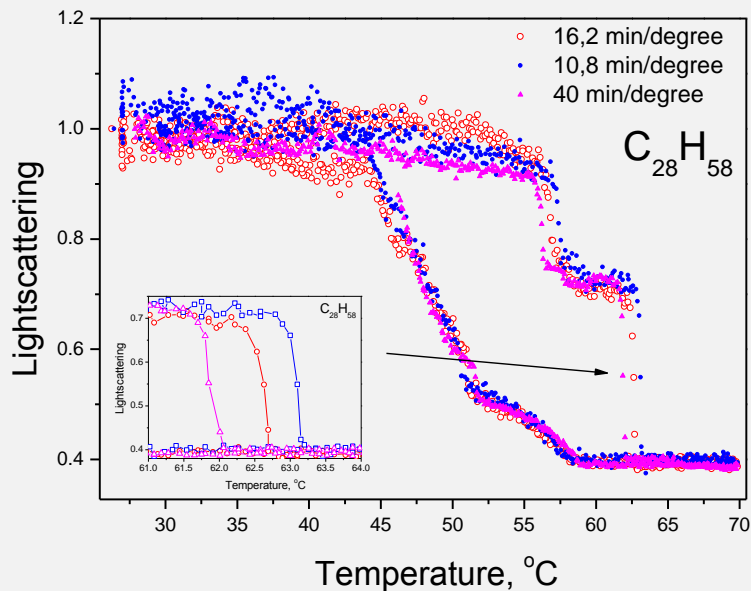
Light scattering temperature dependence for Tricosane

$C_{28}H_{58}$ Octacosane

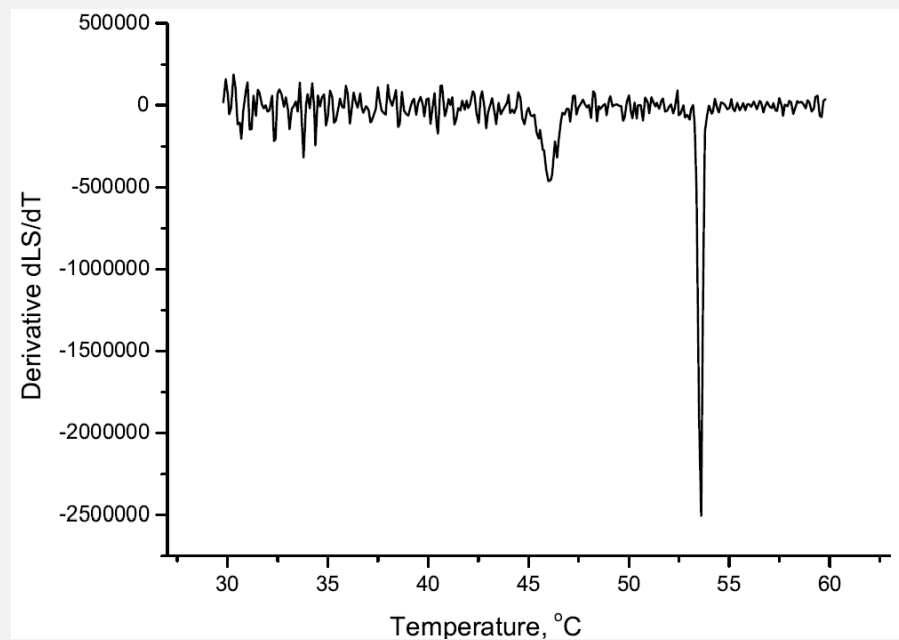
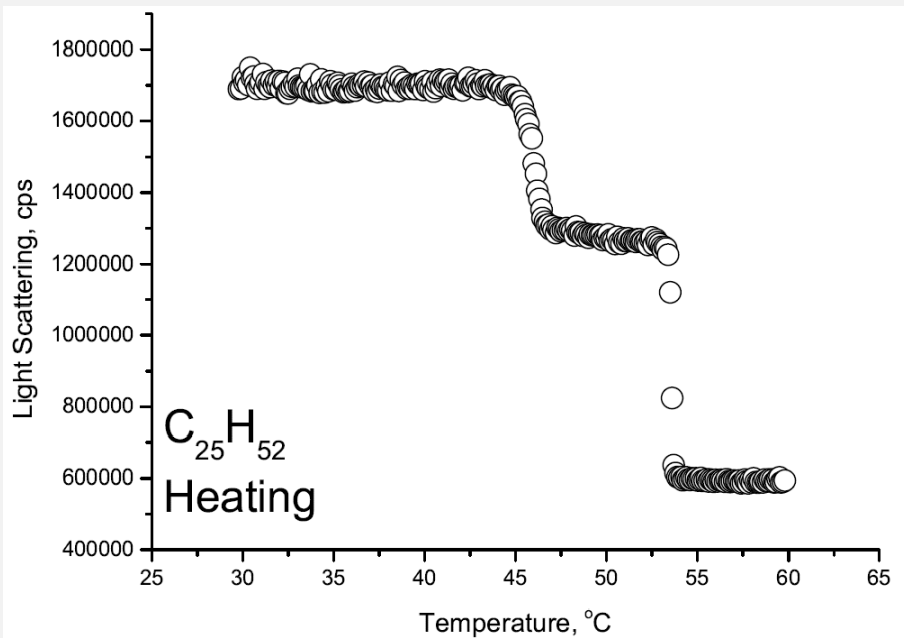


Light scattering temperature dependence for Octacosane

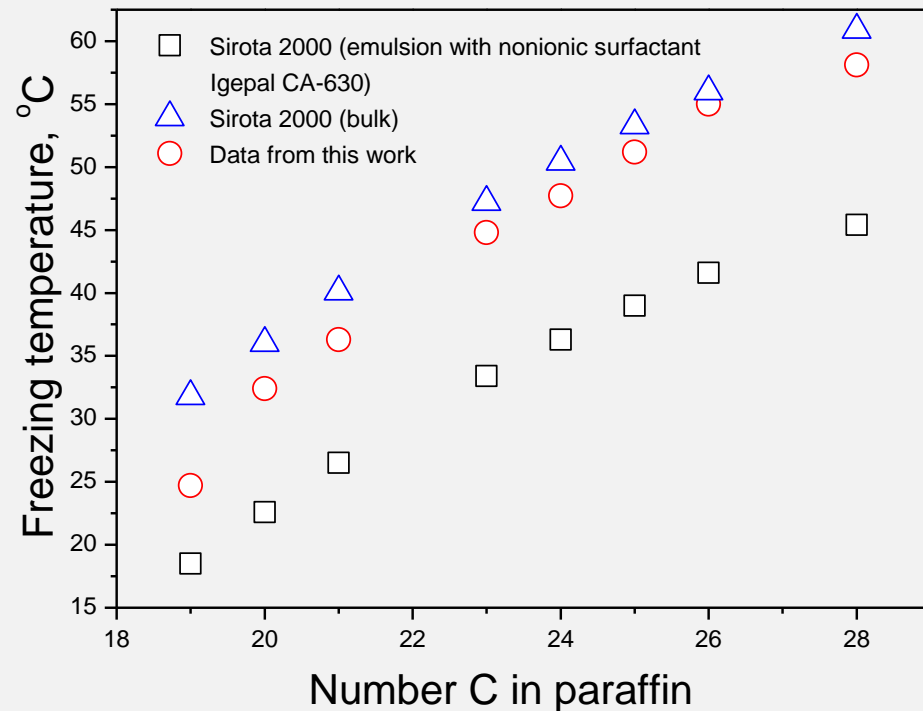
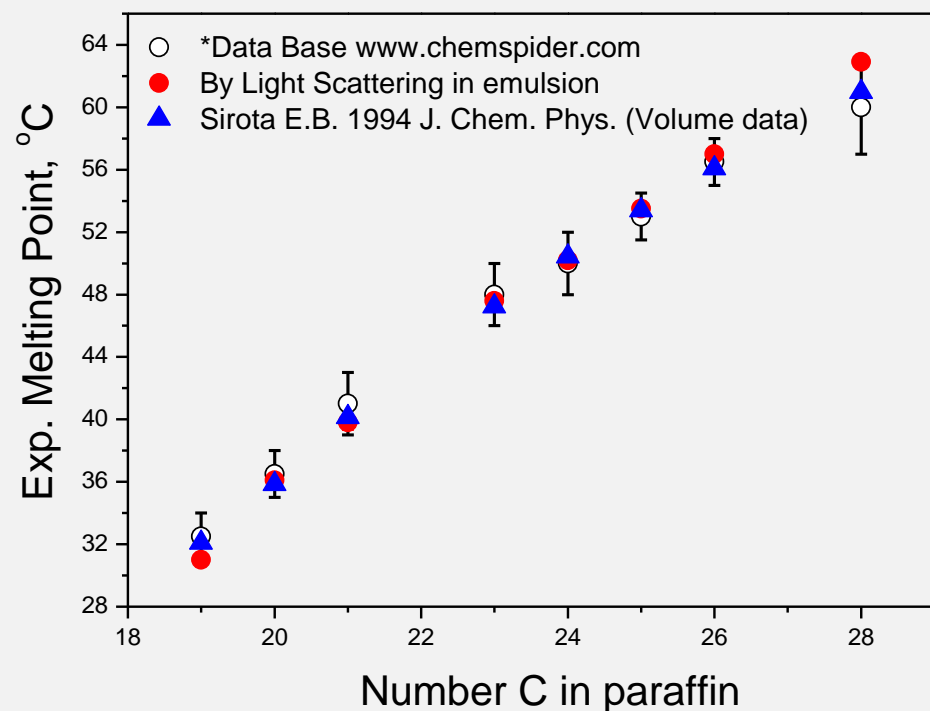
Reproducibility of results



Data analysis



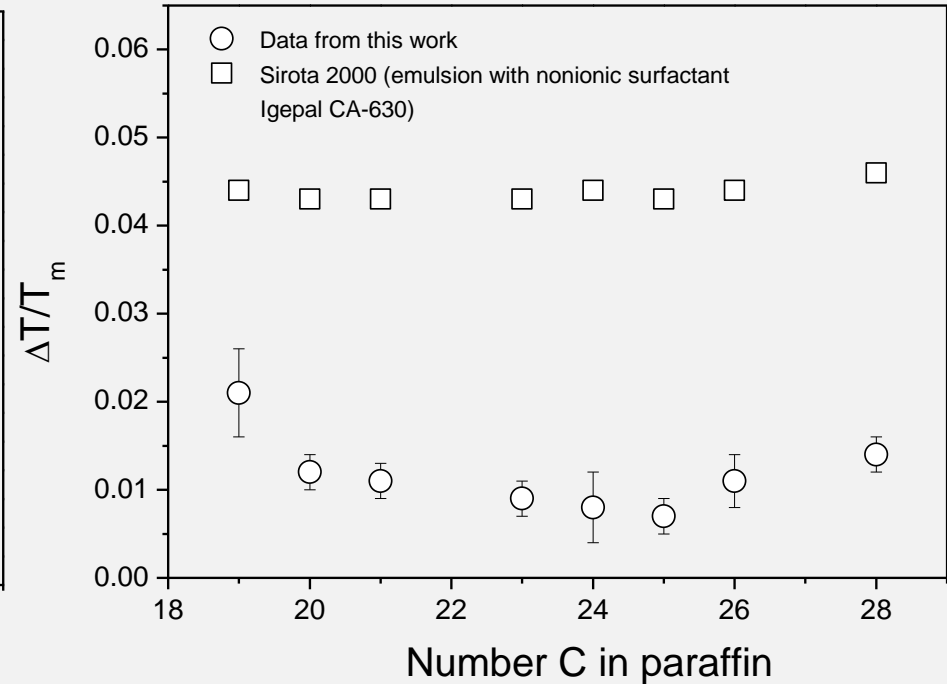
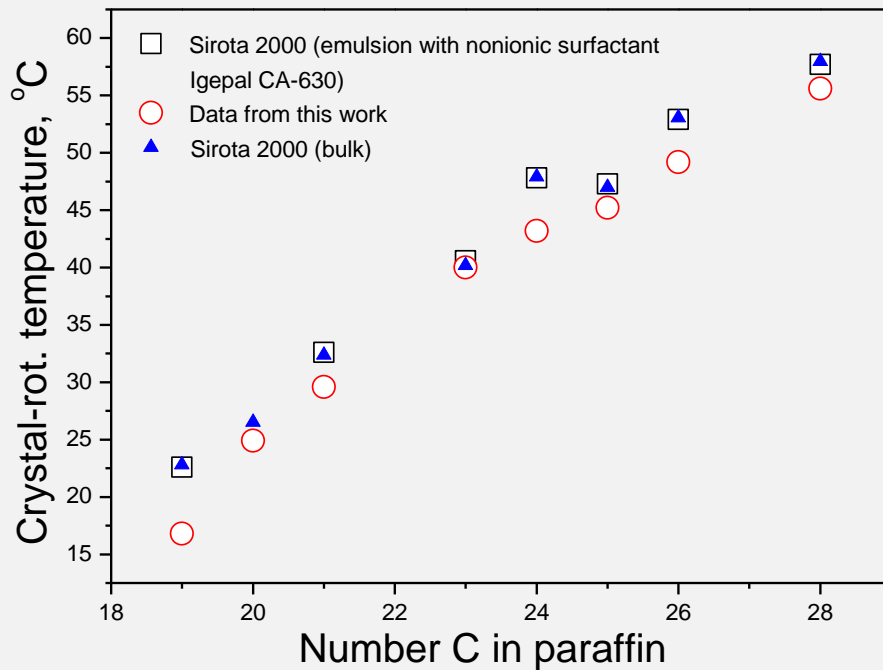
Temperatures of phase transitions



Experimental melting temperatures and freezing temperatures (liquid to rotator)

*www.chemspider.com Experimental data of MP from Alfa Aesar, Indofine, Oxford University Chemical Safety Data, Merck Millipore, Jean-Claude Bradley Open Melting Point Dataset

Temperature of phase transitions

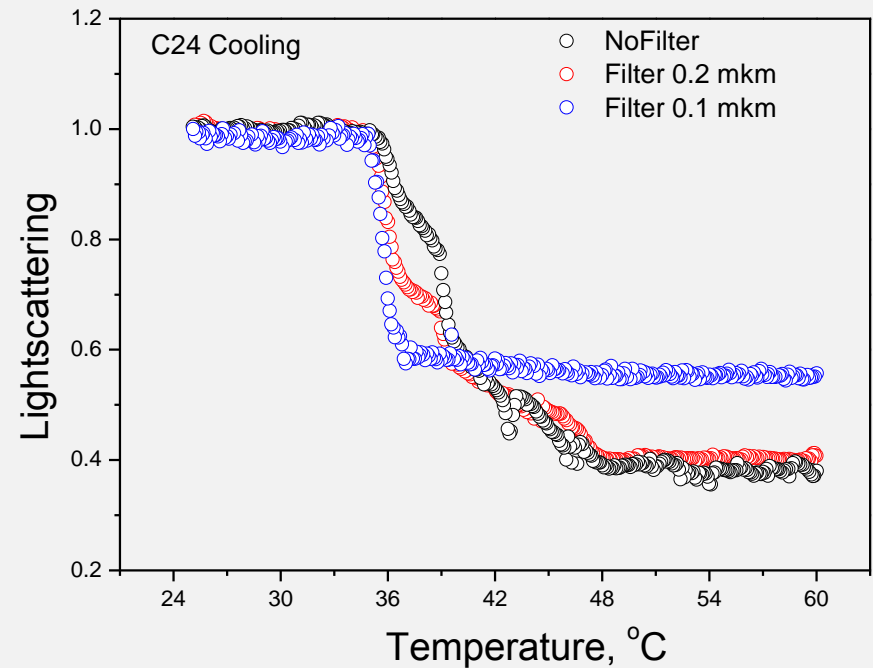
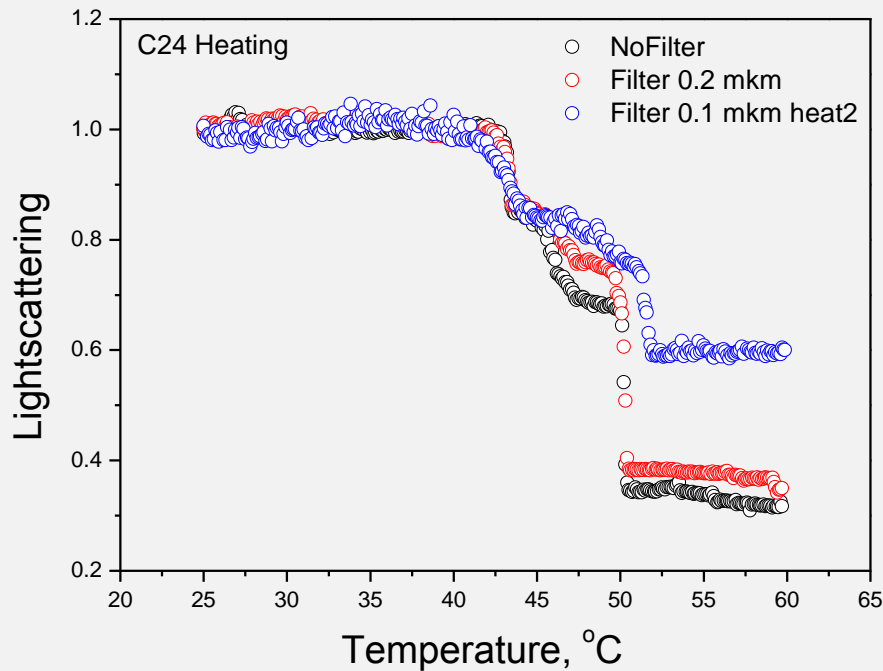


Temperatures of crystal to rotator phase transitions and relative emulsion undercooling for different paraffins (dT/T_m)

Turnbull and Cormia's pioneering work showed that from C_{16} to C_{32} the relative undercooling for homogeneous nucleation, $\Delta T/T_m$, is ~ 0.04 instead of the ~ 0.2 common to most organic materials.

Sirota E.B. microemulsion samples: "Mean diameter of emulsion 4 to 5 μm and an average deviation from the mean of 50%–70%." More than ten times bigger than in this work. Sirota E.B. J. Chem. Phys., Vol. 112, No. 15, 15 April 2000

Suppression of phase transition



Light scattering temperature dependence for Tetracosane. Different size of droplets. Suppression of phase transition at cooling in droplets $R < 50$ nm. This sample has been pre-filtered through 0.1 mkm filter

Conclusions

- Stable emulsions of the oil-in-water type have been prepared without the use of surfactants
- High sensitivity and resolution of measurements enables us to determine temperatures of phase transitions at concentrations down to 10^{-6} weight % paraffin in water
- Suppression of a phase transition is observed for droplets with a size less than 50 nm
- The method of dynamic and static light scattering can not only measure the size of paraffin emulsions, but also determine the temperatures of different paraffin phase transitions in the emulsion

Related publications:

Kuryakov V N, Ivanova D D and Kienskaya K I 2020 Study of the physicochemical characteristics of dispersions of n-alkanes C₂₃H₄₈ and C₂₈H₅₈ in water: zeta potential and temperatures of phase transitions *Russ. Chem. Bull.* 69 1306–10

Kuryakov V, Zaripova Y, Varfolomeev M, De Sanctis Lucentini P G, Novikov A, Semenov A, Stoporev A, Gushchin P and Ivanov E 2020 Comparison of micro-DSC and light scattering methods for studying the phase behavior of n-alkane in the oil-in-water dispersion *J. Therm. Anal. Calorim.*

Kuryakov V N, Ivanova D D, Semenov A P, Gushchin P A, Ivanov E V., Novikov A A, Yusupova T N and Shchukin D 2020 Study of Phase Transitions in n-Tricosane/Bitumen Aqueous Dispersions by the Optical Method *Energy & Fuels* 34 5168–75

V.N. Kuryakov, D.D. Ivanova, Crystallization Behavior of Pure N-Alkane (N-Nonadecane) in a Form of Nanoemulsion, *Int. J. of Nanoscience*, (2019)

V.N. Kuryakov, D.D. Ivanova, Determination of melting point of n-alkanes by means of light scattering technique, *J. of Physics: Conference Series*, (2019)