Extending the Capability of Pulsed NMR Instruments to Measure Solid Fat Content as a Function of Both Time and Temperature

Sir:

We describe modifications to a pulsed NMR (p-NMR) instrument that allow us to measure solid fat content (SFC) as a function of the cooling rate of a lipid sample. This modification is being shared with the lipid community, as it extends the capability of the instrument to reveal previously inaccessible parameters of the crystallization process relating to processing conditions.

The rate of cooling may cause changes in the growth mode of the network and can lead to polymorphic, microstructural, and SFC changes, and thus changes in the final physical properties of the network (1,2). p-NMR has been used to determine the shape of the crystallization curve, final solids content, and induction time of crystallization. The measurement of induction time by p-NMR is flawed because before the instrument can record a measurement, the sample must contain approximately 1% solid fat (i.e., the initial nucleation has already occurred) (3). Owing to this flaw, a comparison of the variation of induction time as a function of cooling rate would provide a relative measure of the variation of the activation free energy of nucleation as a function of cooling rate. Measures of induction time are significant, as they may be used in the Fisher–Turnbull model to calculate activation energies of nucleation (4,5). It is important to note here that activation energies so calculated can only be compared as a *relative* measure, since true nucleation has already occurred. Furthermore, the shape of the crystallization curve and the final solids content of the lipid material as a function of cooling rate would provide valuable insight into the thermodynamic dependence of crystallization and would suggest ways in which molecular ensembles can be processed to achieve desired results. However, until now, it has been difficult to achieve a wide variety of cooling rates within a p-NMR cell, owing to the inability of a single programmable circulating bath to achieve cooling rates higher than 5°C/min.

The p-NMR used in our laboratory is a "minispec mq SFC analyzer," manufactured by Bruker Optics (Milton, Ontario). The measurement chamber's temperature is controlled by an external circulating bath. We have devised the manifold arrangement shown in Figure 1, which allows us to use multiple baths to increase the temperature gradients that we can achieve within the p-NMR cell. A maximum of six baths can be connected to the NMR *via* the manifold system of hoses and butterfly valves shown. Thus, it is possible to cool the NMR with bath A and, by shutting off two valves and opening two others, change the flow to that from bath B almost instantaneously.

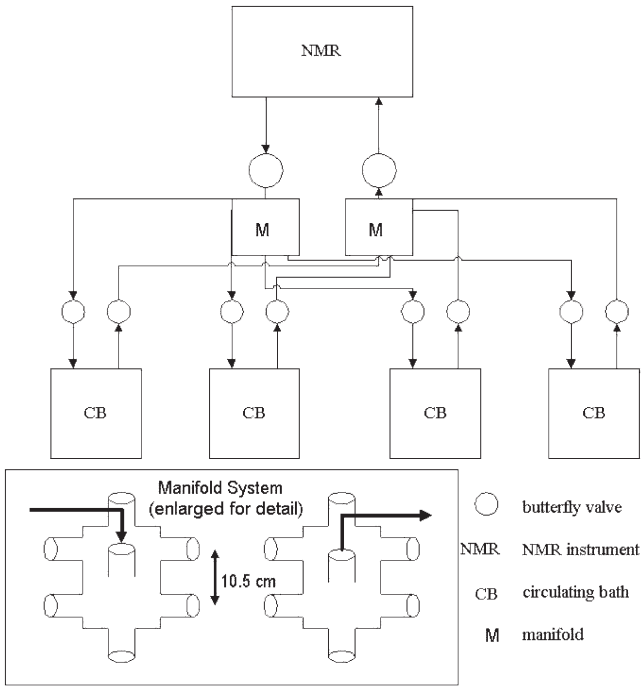

FIG. 1. Diagrammatic representation of the NMR cooling device.

Flexible hoses and stainless steel pipes, both with inner diameters of 9.5 mm, were used in the construction of the manifold system. The hoses that connect the manifold to the NMR are 64 cm, and those connecting the baths to the system are 97 cm. The hoses, stainless steel manifold, and butterfly valves were insulated with 1-cm pipe insulation. The bath's coolant was a 60:40 glycol-to-water mixture, with flow rates of 4.5 to 8.5 L/min.

To attain a given cooling rate, it is necessary to create the appropriate temperature gradient between the bath and the p-NMR chamber. This is achieved using a combination of baths. The system is first calibrated with highly unsaturated oils such as canola oil (with heat capacities similar to more saturated oils, but which do not crystallize until –20°C). For example, to achieve a cooling rate of 10°C/min, the sample is equilibrated at 67°C and then placed in the p-NMR chamber

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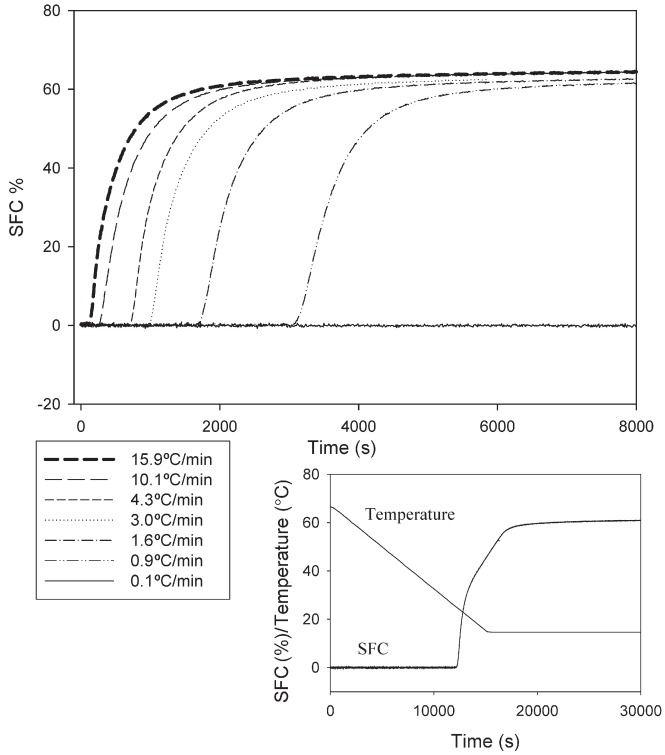

FIG. 2. Solid fat content (SFC) vs. time for various cooling rates with inset SFC/temperature vs. time with 0.1°C/min cooling rate.

at 35°C for 66 s, moved to a bath at −10°C for 272 s, and then to a final sample temperature bath of 13.5°C for 120 s.

The temperature gradient between any bath and the p-NMR cell is dependent on the size of the reservoir in the bath, the rate at which the glycol–water mixture is pumped, and the reduction in flow due to conducting hoses. Thus, after calibration, it is essential to maintain the configuration of hoses, baths, the order in which the various baths are used, and the amount of sample used (2.5 ± 0.1 g). Another factor is the choice of bath used. For example, if the system is equilibrated at 35°C and is then connected to a bath at −10°C, the −10°C bath must have a high cooling capacity, as opposed to the situation where the system at 35°C is connected to a bath at 20°C.

Figure 2 shows the variation in SFC over time with the same ensemble of lipid molecules and seven cooling rates of 0.1 to 15.9°C/min within the p-NMR cell. The fat sample used was a commercial lipid product, used as a coating fat, manufactured by Bunge Foods Ltd. (Bradley, IL). As the cooling rate increases, the onset time of crystallization decreases (as is to be expected when the crystallization temperature is much lower than the melting temperature, i.e., under conditions of high supercooling). Faster cooling rates result in much higher levels of supercooling, under conditions that are decidedly nonisothermal, since crystallization is going on, but the temperature is still being decreased. The inset shown in Figure 2 is a graph of a typical temperature profile and corresponding SFC profile of the sample.

Therefore, the use of this device allows one to measure the SFC of a lipid sample as a function of temperature so as to determine the induction time, shape of the crystallization curve, total crystallizing time, and final SFC as a function of cooling rate.

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