Supplementary information

Insight into the cryopolymerization to form poly(N-isopropylacrylamide) / clay macroporous gel. Structure and phase evolution

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Experimental

Differential scanning calorimetry

Due to the fact that the samples never totally crystallize, it was not possible to discern the contributions of ice and of crystalline NIPA to the total melting enthalpy of the sample. Therefore, for an estimate of the fraction of ice, we assumed that the measured enthalpy of melting stems from the ice melting only (this is acceptable in view of the relatively low concentration of NIPA, and of its low melting enthalpy in comparison to ice).

The concentration of NIPA in the non-frozen liquid phase is given by formula:

$$w_{NIPA} = \frac{w_{NIPA}^o}{w_{NIPA}^o + w_{NIPA}(1 - \frac{\Delta H_{exp}^m}{\Delta H_{m,water}^o})}$$

where $w_{NIPA}^o$ is the weight fraction of NIPA in the initial NIPA solution.

Results and Discussion

3.1. Cryostructuration
**Fig. SI 1** $^1$H NMR spectrum of the 8.5 wt.% NIPA solution in H$_2$O/D$_2$O (80/20) mixture at cooling (a) $T= 15 \, ^\circ C$, (b) $T= -8 \, ^\circ C$, prior to crystallization, (c) $T= -13.5 \, ^\circ C$, after crystallization. Mixture H$_2$O/D$_2$O (80/20) was used as the solvent in this case in order to detect better the signal of residual water also after freezing. The peaks assignment of NIPA and water is described in the figure.

**Fig. SI 2** Mobile fraction of water (■) and NIPA (○) as a function of temperature. NIPA/D$_2$O solution (8.5 wt. % of NIPA). Virtually the same dependence was obtained for various proton groups of NIPA.
3.1.1. Phase evolution of NIPA solution during cryostructuration

Fig. SI 3  The heat flow (a) and temperature (b) as functions of cooling time at heterogeneous crystallization of mixtures NIPA/H$_2$O and NIPA/clay/H$_2$O. Samples cooled at a cooling rate 1 °C/min.

B,C,E – points correspond to the phase diagram in Fig.2

3.2. Cryopolymerization
3.2.1. Kinetics of cryopolymerization

Steric confinement
The polymer mobility is revealed from Fig. SI4 displaying $^1$H NMR spectra taken during polymerization of NIPA (Fig. SI4 a,b) and the NIPA/clay system (Fig. SI4 c,d) at $T= -10 \, ^\circ C$ prior and after water crystallization.

Fig. SI 4 $^1$H NMR spectra of NIPA and NIPA/clay polymerization mixtures in D$_2$O at $T= -10 \, ^\circ C$. a) PNIPA unfrozen solution, b) PNIPA semi-frozen solution, c) PNIPA/clay unfrozen solution, d) PNIPA/clay semi-frozen solution. P–polymer, N–NIPA, T–TEMED.

The polymer is characterized by the broader signals which are designated by P. The peaks at 2.22 and 2.50 ppm correspond to the activator TEMED.

### 3.2.2 Phase changes and reaction progress during cryopolymerization

Fig. SI 5 Heat of reaction during polymerization of NIPA at $T= -20 \, ^\circ C$. Dash line indicates the baseline determined by subtraction of crystallization.