Domain formation behavior of high pressure rotator phase of n-tridecane, pentadecane and heptadecane studied by FT-IR

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The effect of pressure on the phase transition behavior of tridecane (C\textsubscript{13}), pentadecane (C\textsubscript{15}) and heptadecane (C\textsubscript{17}) has been investigated up to 489, 220 and 387 MPa, respectively, using Fourier transform infrared spectroscopy at 25 °C. The transition between the high pressure ordered (HPO) and high pressure rotator (HPR) phase has been observed in the pressure ranges of 270–220, 106–95 and 152–181 MPa for C\textsubscript{13}, C\textsubscript{15} and C\textsubscript{17}, respectively, and the transition between the HPR and liquid phase was observed in the pressure ranges of 171–112, 73–47 and 43–70 MPa for C\textsubscript{13}, C\textsubscript{15} and C\textsubscript{17}, respectively. The P\textsubscript{1}+P\textsubscript{3} band of the methylene rocking mode exhibits factor group splitting caused by intermolecular vibrational coupling. This was observed in both the HPO and HPR phases, while the P\textsubscript{1}+P\textsubscript{3} band did not split in the liquid phase. The separation of the peaks in the P\textsubscript{1}+P\textsubscript{3} band changed discontinuously at the HPO-HPR and HPR-liquid phase transitions, even though the separation is known to change continuously in the transition from the liquid to the high temperature rotator (HTR) phase. In the HPR phase, the ratio of the intensities of the higher and lower frequency components in the P\textsubscript{1}+P\textsubscript{3} doublet is roughly unity independent of pressure, while it is known to be much less than unity in the HTR phase. From the intensity ratio, a large proportion of alkane molecules are believed to participate in intermolecular vibrational coupling and possess herringbone-type short-range positional order in the HPR phase. Conversely, in the HTR phase only small proportion of alkane molecules participate in intermolecular vibrational coupling. From the pressure dependence of the separation of the doublet, intermolecular vibrational coupling and herringbone-type short-range positional order is considered to change discontinuously at the HPR-liquid phase transition, while they are reported to change continuously at the HTR-liquid phase transition. The HPR-liquid phase transition is governed by the effect of molecular packing while the HTR-liquid phase transition is predominantly governed by the difference in entropy between the herringbone-type and parallel-type packing.