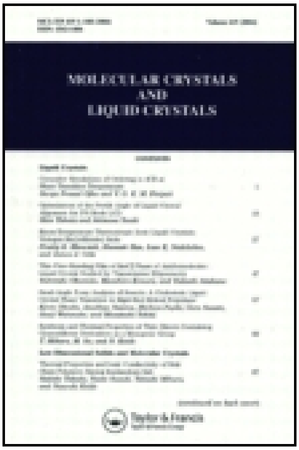

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Mesophases of Alkylammonium Salts III. Disorder and Motion in the Intermediate Homologs: $[CH_3(CH_2)_{n-1}]_4NX$, n = 4, 5, 6, 7 and X = Br and I

Jinlong Cheng [a b] , Alexander Xenopoulos [a b] & Bernhard Wunderlich [a b]

[a] Department of Chemistry, University of Tennessee, Knoxville, TN, 37996-1600

[b] Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6197

Version of record first published: 24 Sep 2006.

To cite this article: Jinlong Cheng , Alexander Xenopoulos & Bernhard Wunderlich (1992): Mesophases of Alkylammonium Salts III. Disorder and Motion in the Intermediate Homologs: $[CH_3(CH_2)_{n-1}]_4NX$, n = 4, 5, 6, 7 and X = Br and I, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 220:1, 127-157

To link to this article: http://dx.doi.org/10.1080/10587259208033435

Mol. Cryst. Liq. Cryst., 1992, Vol. 220, pp. 127–157
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Mesophases of Alkylammonium Salts III. Disorder and Motion in the Intermediate Homologs: $[CH_3(CH_2)_{n-1}]_4NX$, $n = 4, 5, 6, 7$ and $X = Br$ and I

JINLONG CHENG, ALEXANDER XENOPOULOS and BERNHARD WUNDERLICH†
Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 and Chemistry Division of Oak Ridge National Laboratory, Oak Ridge, TN 37831-6197

(Received February 4, 1992)

Disorder and motion in crystals and mesophases of tetra-*n*-alkylammonium halides of intermediate chain length alkyl groups, $[CH_3(CH_2)_{n-1}]_4NX$, where $n = 4, 5, 6, 7$ and $X = Br$ and I, have been analyzed based on entropy changes of phase transitions known from differential scanning calorimetry (DSC) and new measurements of solid state ^{13}C nuclear magnetic resonance spectra (NMR). Some mesophase transitions from the crystal state involve only conformational motion and disordering to lead to condis crystals. The conformational motion and disordering in the alkyl chains may also be introduced gradually (transitionless change to a condis crystals). Further heating of the samples increases the degree of conformational disorder (entropy) to reach different, more disordered condis states, or causes orientational motion and disorder of the cation as a whole to form plastic crystals, which in this intermediate alkyl chain-length group of salts contain always conformational disorder. Finally, isotropization occurs either directly from the condis state or out of the plastic crystal.

Keywords: tetra-n-alkylammonium bromides and iodides, disorder and motion, plastic crystal, condis crystal, solid state ^{13}C NMR, thermal analysis

INTRODUCTION

In the first paper of this series of publications,[1] the thermal properties of symmetric tetra-*n*-alkylammonium salts were discussed based on the concept of orientational and conformational motion and disorder. This work led to the suggestion that the salts of intermediate alkyl-chain length cations, studied in this paper, may show both plastic and condis crystal phases. This behavior is unique to the intermediate length tetra-*n*-alkylammonium cations. The shorter-chain salts have no confor-

---

†The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

mationally disordered phases, while the longer ones have no orientationally disordered phases.

Conformational disorder can be introduced only to the bonds that are separated from the nitrogen by two or more carbon atoms. The two inner-most bonds are restricted to a single rotational isomer. Rotations about the CH_2—CH_3 bond is, in contrast, so facile that it starts rotating at very low temperature, but its rotation about the C_3 axis does not alter the overall molecular shape. Thus, the number of bonds that can be disordered per alkyl chain in the intermediate and long-alkyl chain length tetra-*n*-alkylammonium salts is $n - 3$, where n is the number of carbon atoms. This generalization was made based on the study of the low-homologs of tetra-*n*-alkylammonium halides,[2] which form plastic crystals without conformational disorder as their only mesophases.

In this paper a study of the orientational and conformational motion and disorder is reported for the tetra-*n*-alkylammonium bromides and iodides with 4 to 7 carbon atoms per chain. It will be shown that conformational disordering in the intermediate-length alkyl-chain cations tends to take place first in the outer bonds (close to the chain end), and develops towards the inner bonds as the temperatures is increased, leading to stepwise conformational disordering. The conformational disordering may sometimes occur gradually without recognizable transition, starting also from the chain end. In this case, an entropy deficit is expected when adding the transition entropies from the crystal to the melt.

Experimental details of conformational motion and disorders in $[CH_3(CH_2)_{n-1}]_4NX$, $n = 4, 5, 6, 7$ and X = Br and I, will be provided in this paper by mainly two ^{13}C NMR observables, namely, the chemical shifts and the spin-lattice relaxation times (T_1). Both were monitored as a function of temperature. The entropy data[1] obtained before are discussed together with the NMR results and will be shown to be supplementary and consistent.

EXPERIMENTAL

The samples used in this paper have been described in detail in the first paper of this series of publications.[1] They consisted of commercially produced bromides and iodides of $[CH_3(CH_2)_{n-1}]_4NX$ with $n = 4, 5, 6$, and 7. All samples had purities in the 99% range and were used as received. Solution NMR did not detect any proton and carbon containing impurities.

All solid state ^{13}C NMR measurements were made with a Nicolet NT 200 spectrometer operating at 200.07 and 50.31 MHz for ^1H and ^{13}C, respectively. The solid state probe was purchased from Doty Scientific, Inc. The probe has variable temperature capability over the range of 120–430 K. Temperature calibration below and above 300 K was done by measuring the proton resonances of liquid methanol and ethylene glycol,[3] respectively. The cylindrical sample container (rotor) was made from a single crystal of Al_2O_3 (sapphire) and has a diameter of 5 mm. The end cap pairs used for the rotor were made from brown, plastic Vespel® (Registered trademark for a DuPont polyimide). The sample was spun with nitrogen gas at 4.5 kHz at the magic angle for all measurements below 300 K. After stabilizing temperature and sample spinning rate, prior to each measurement, the probe was tuned and matched with a 2382 Spectrum Analyzer (100 Hz—400 MHz) made by Marconi Instruments.

At the temperatures where condis crystals exist or lower, the ^{13}C NMR spectra were measured with the combined techniques of *cross-polarization* (CP), *high-power decoupling of protons*, and *magic angle sample spinning* (MAS), known as CP-MAS. The ^{13}C chemical-shift-anisotropy powder patterns were obtained on the static samples with CP and high-powder decoupling. The spin-contact time was typically 1–3 ms. The 90° pulse-width for the proton was 4.75 μs, which results in a decoupling field of about 53 kHz. For plastic crystals with conformational mobility, on the other hand, the ^{13}C NMR spectra were only measurable with the pulse sequence for liquids, namely, one-pulse for ^{13}C with two-level decoupling of protons (BILEV). The ^{13}C spin-lattice relaxation times (T_1) were measured using *progressive saturation* method for $T_1 \geqslant 10$ s or *inversion recovery* for $T_1 < 10$ s. The 90° and 180° pulse-width used for ^{13}C T_1 measurements were 4.15 and 8.30 μs, respectively. The reported ^{13}C chemical shifts were relative to tetramethylsilane (TMS) by calibrating with hexamethylbenzene [the methyl carbon has a chemical shift of (17.35 ± 0.20) ppm].

RESULTS

Tetra-*n*-butylammonium Bromide and Iodide

The variable temperature ^{13}C NMR spectra of the bromide are plotted in Figure 1 along with a solution ($CDCl_3$) spectrum. Below the lowest disordering transition (367.0 K), the large-amplitude motion is practically quenched, the ^{13}C NMR spectra are only measurable with the CP-MAS method; at temperatures close or above isotropization (393.9 K), the molecular motion is so rapid that the ^{13}C NMR spectra become no longer observable with CP-MAS, and the pulse sequence for the liquid-like samples (BILEV) had to be used; while at some intermediate temperatures (condis phase) both CP-MAS and BILEV are applicable. The same holds true for all other compounds studied in this work. Some numerical values of the chemical shifts of Figure 1 are listed in Table I along with that of the solution spectrum taken at room temperature.

The variable-temperature ^{13}C NMR spectra for the iodide are shown in Figure 2. A drastic change in the chemical shifts can be seen going to the 395 and 402 K spectra. This change corresponds to the disordering transition observed in DSC at 394.0 K with an entropy change of 71.2 JK^{-1} mol^{-1}. The spectra above 394.0 K become no longer observable with CP-MAS, but are measurable with BILEV. The numerical values of the chemical shifts are listed in Table II. The variable-temperature ^{13}C chemical-shift-anisotropy powder patterns are graphed in Figure 3.

The ^{13}C spin-lattice relaxation times of the bromide were measured at 384 K with the *progressive saturation* method, the results for C-2, C-3 and C-4 are 10, 1.51, and 2.58 s, respectively. The T_1 for C-1 is not available at 384 K because the resonance of C-1 is rather weak due to the line-broadening. The T_1-values for the iodide were measured at 308, 329 and 408 K and are listed in Table III. Included

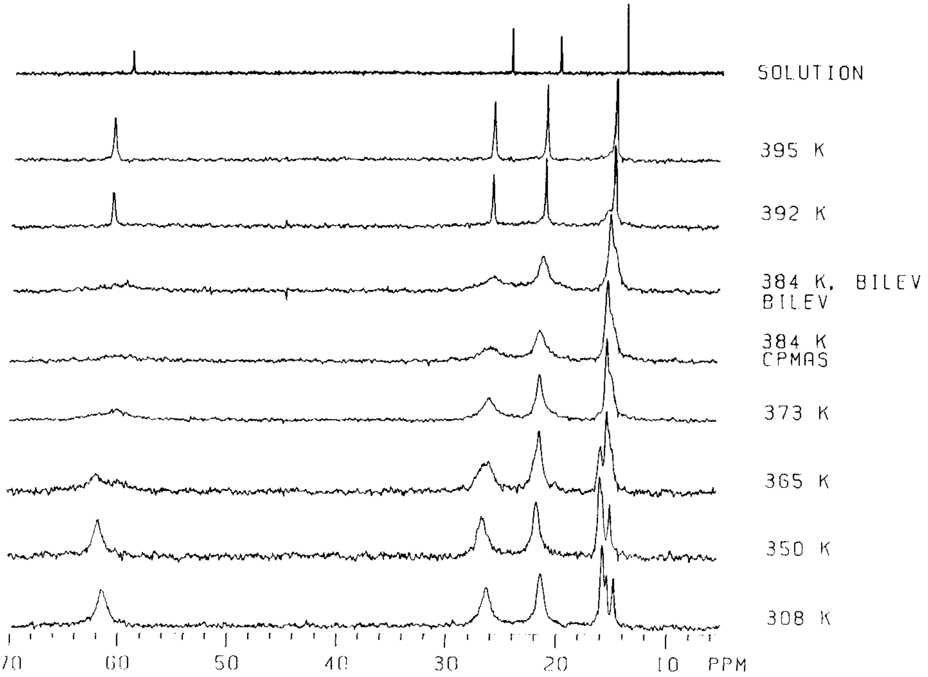

FIGURE 1 ^{13}C NMR spectra of tetra-*n*-butylammonium bromide at, from bottom to top: 308, 350, 365, 373, 384 K, obtained with CP-MAS (the pulse sequence for rigid materials), and at 384, 392, and 395 K, measured with BILEV (the conventional pulse sequences for solution). Two spectra were obtained for the condis state of 384 K, labeled as BILEV and CPMAS. The top spectrum is measured in $CDCl_3$ solution at room temperature. Some chemical shifts are listed in Table I.

in the table are also the T_1-values for $(C_4H_9)_4NClO_4$ measured in CD_3OD solutions by Coletta *et al.*[4]

Tetra-*n*-Pentylammonium Bromide and Iodide

Figures 4 and 5 show the variable temperature ^{13}C CP-MAS spectra for the bromide and the iodide, respectively. The chosen temperatures cover all observed solid-mesophase transitions [(374 K for $(C_5H_{11})_4NBr$, 404.6 and 412.1 K for $(C_5H_{11})_4NI$)]. The chemical shift values at the selected temperatures are listed in Tables IV and V. For tetra-*n*-alkylammonium salts with chains consisting of 5 or more carbon atoms, the chemical shift value of a given carbon atom is no longer determined solely by its proximity to the nitrogen. For example, in the solution state C-2 has a smaller chemical shift than all others carbon atoms, except the methyl group carbon, as can be seen in Tables IV and V and the subsequent tables for longer chain salts.

The relaxation times of each individual carbon atom at different temperatures are listed in Tables VI and VII for the bromide and iodide, respectively.

Tetra-*n*-hexylammonium Bromide and Iodide

The ^{13}C MAS NMR spectra of tetra-*n*-hexylammonium bromide at temperatures above room-temperature are shown in Figure 6. The low temperature spectra (from

TABLE I

^{13}C NMR chemical shifts in tetra-*n*-butylammonium bromide at some typical temperatures (in ppm relative to TMS)[a]

Temperature (K)	C-1	C-2	C-3	C-4 (Methyl)
308	61.47	26.31	21.39	15.61/15.30/14.70
Disordering transition: T_d = 367.0 K, ΔS_d = 41.2 JK^{-1}mol^{-1}				
373	61.37/59.84	25.63	21.09	14.96/14.47
Transition: 379.2 K, 1.4 JK^{-1}mol^{-1}				
384	NA[b]	25.74	21.09	14.97/14.49
Isotropization: T_i = 393.9 K, ΔS_i = 37.6 JK^{-1}mol^{-1}				
395 (melt)	60.45	25.57	20.74	14.41
Solution (in $CDCl_3$)	59.09	24.23	19.79	13.74

[a] Spectra of Fig. 1. Multiple values are given for carbon atoms having more than one peak.

[b] NA stands for data not available, because of broadness and weakness of the resonance.

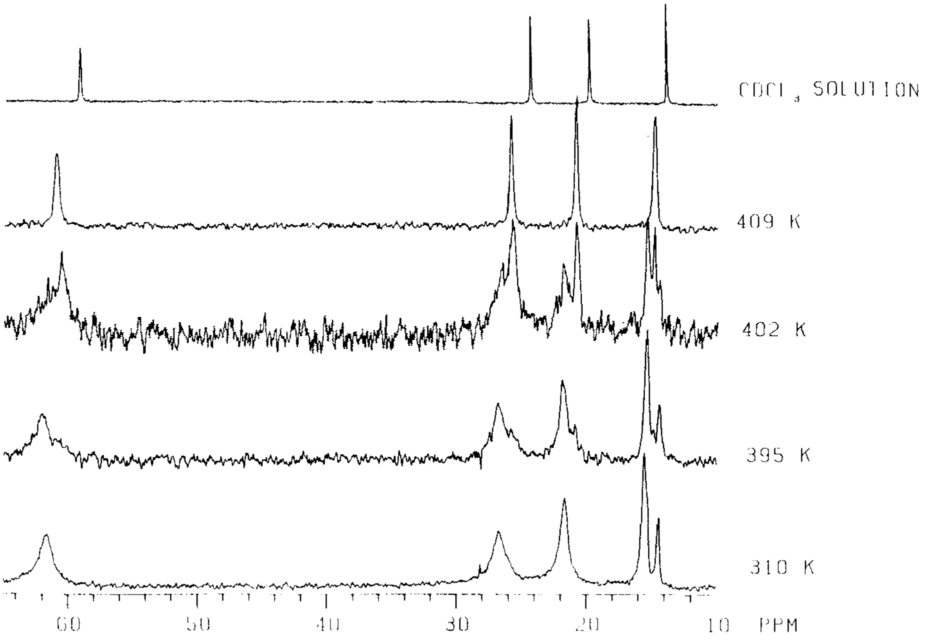

FIGURE 2 ^{13}C NMR spectra of tetra-*n*-butylammonium iodide at 310 K obtained with CP-MAS, and, from bottom to top: 395, 402, and 409 K, with BILEV. The top spectrum is measured in $CDCl_3$ solution at room temperature. The chemical shifts are listed in Table II.

TABLE II

^{13}C NMR chemical shifts in tetra-*n*-butylammonium iodide as a function of temperature (in ppm relative to TMS)[a]

Temperature (K)	C-1	C-2	C-3	C-4 (Methyl)
310	61.58	26.67	21.65	15.53/15.32/14.40
387	61.91	26.79	21.77	15.36/15.36/14.37
Disordering transition: T_d = 394.0 K, ΔS_d = 71.2 JK^{-1}mol^{-1}				
395	62.09	26.78/25.85	21.87/20.90	15.33/14.79/14.39
402	60.63	26.52/25.80	21.87/20.85	15.34/14.97/14.43
409	60.97	25.84	20.80	14.67
416	61.00	25.85	20.79	14.64
Isotropization: T_i = 420.6 K, ΔS_i = 21.3 JK^{-1}mol^{-1}				
Solution (in $CDCl_3$)	59.32	24.40	19.84	13.78

[a] Spectra of Fig. 2 and additional spectra at 387 and 416 K. Above the disordering transition temperature (394 K), the spectra are only detectable with the pulse sequences for liquids (BILEV). Multiple values indicate double or triple peaks.

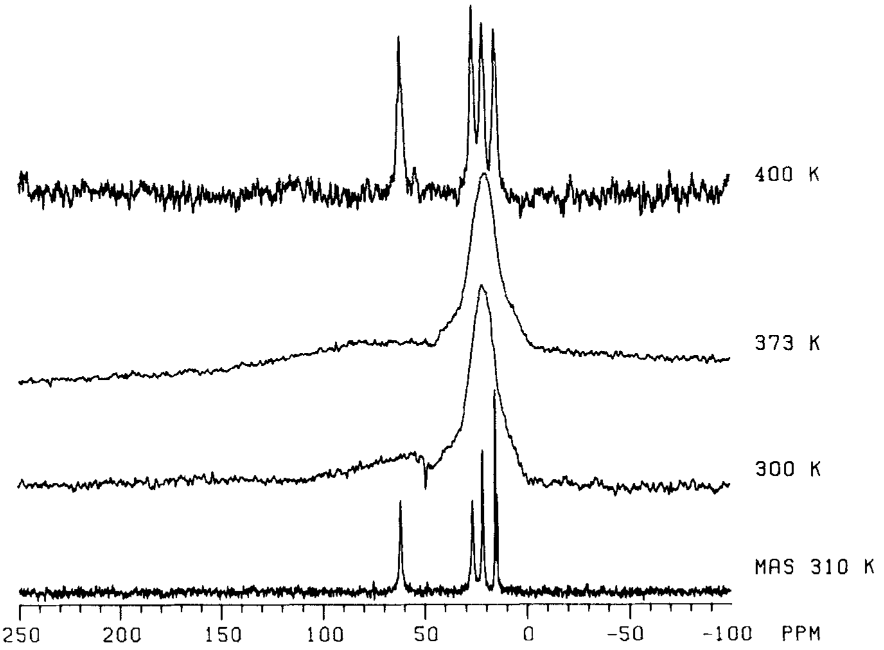

FIGURE 3 Variable temperature ^{13}C NMR powder patterns of tetra-*n*-butylammonium iodide obtained at 300, 373, and 400 K. The bottom trace is the CP-MAS spectrum at 310 K to show the isotropic resonance positions.

TABLE III

^{13}C spin-lattice relaxation times of tetra-*n*-butylammonium iodide (in s)[a]

T (K)	C-1	C-2	C-3	C-4[c]
308	56.0 ±1.7	58.5 ±2.1	42.9 ±1.1	1.69 ±0.04; 1.77 ±0.06
329	52.4 ±1.5	60.1 ±3.2	42.3 ±1.0	2.34 ±0.05; 1.89 ±0.08
Disordering transition: T_d = 394.0 K, ΔS_d = 71.2 JK^{-1}mol^{-1}				
408	0.120 ±0.002	0.169 ±0.005	0.514 ±0.010	2.08 ±0.02
Isotropization: T_i = 420.6 K, ΔS_i = 21.3 JK^{-1}mol^{-1}				
Solution[b]	0.4	0.5	0.9	2.3

a Measured with the *inversion recovery* method.

b Data taken from Ref. 4 for the solution of perchlorate salt of tetrabutylammonium ions in CD_3OD, measured at 305 K with a 22.6 MHz (for ^{13}C) spectrometer.

c Data for the methyl carbon are given for the most low- and up-field resonances.

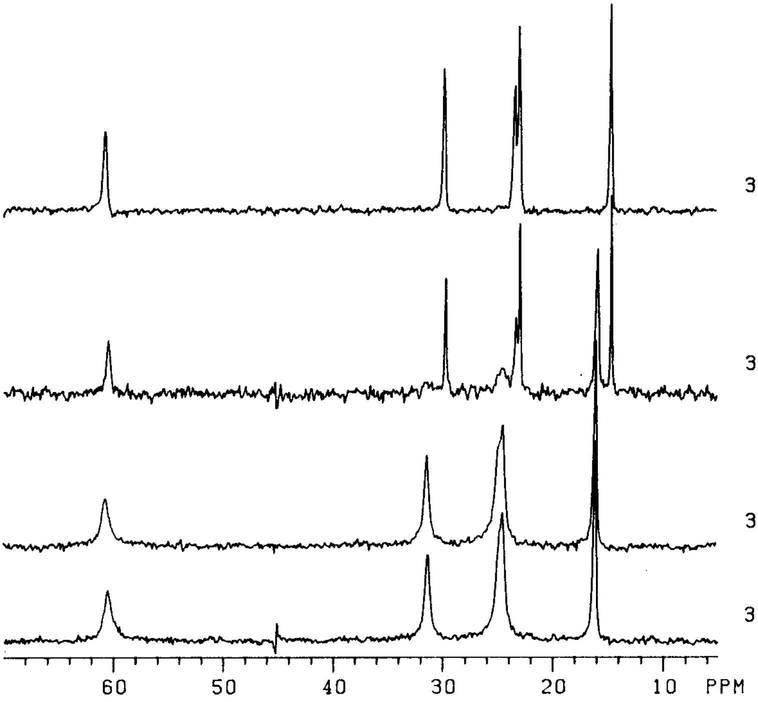

FIGURE 4 ^{13}C NMR spectra of tetra-*n*-pentylammonium bromide obtained with magic angle spinning at, from bottom to top: 308, 341, 373, and 387 K. The chemical shift values including those of the solution are listed in Table IV.

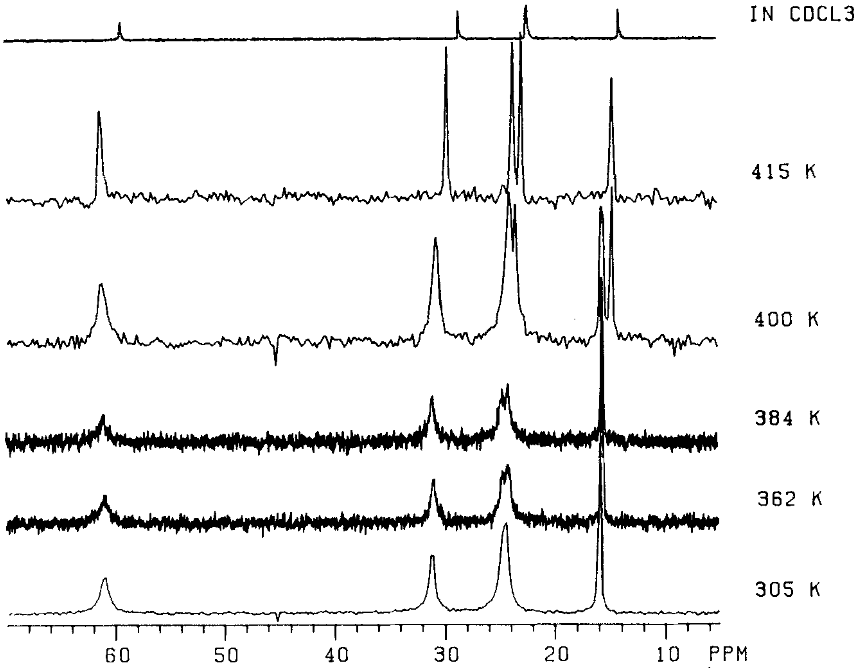

FIGURE 5 ^{13}C NMR spectra of tetra-*n*-pentylammonium iodide obtained with magic angle spinning. The top spectrum is measured in $CDCl_3$ solution at room temperature. The chemical shifts are listed in Table V.

TABLE IV

^{13}C chemical shifts in tetra-*n*-pentylammonium bromide as a function of temperature (in ppm relative to TMS)[a]

T (K)	C-1	C-2	C-3	C-4	C-5
308	60.48	24.60	31.32	24.60	16.14
341	60.57	24.85	31.27	24.42	15.95
Isotropization: T_i = 374.0 K, ΔS_i = 97.9 $JK^{-1}mol^{-1}$					
387	60.63	23.35	29.69	22.92	14.58
Solution (in $CDCl_3$)	59.27	22.06	28.45	22.25	13.83

[a] Spectra of Fig. 4.

about 146 K to 310 K) are shown in Figure 7, obtained on slow cooling (about 10 K/min). Figure 8 shows spectra obtained first on fast cooling (about 60 K/min) from 310 to 146 K, then on slow heating (10 K/min) to 310 K. The variable temperature ^{13}C NMR MAS spectra of $(C_6H_{13})_4NI$ is shown in Figure 9, for temperatures from 308 to 375 K. The chemical shifts based on the variable-temperature

TABLE V

^{13}C NMR chemical shifts in tetra-*n*-pentylammonium iodide as a function of temperature (in ppm relative to TMS)[a]

T (K)	C-1	C-2	C-3	C-4	C-5
305	60.92	24.44	31.05	24.44	15.81
362	60.85	24.15	30.86	24.60	15.54
384	60.87	23.96	30.84	24.56	15.45
400	61.11	23.91	30.52	23.40	15.52/14.71
Disordering transition: T_d = 404.6 K, ΔS_d = 41.2 JK^{-1}mol^{-1}					
Isotropization: T_i = 412.1 K, ΔS_i = 94.0 JK^{-1}mol^{-1}					
415	61.15	23.61	29.63	22.80	14.62
Solution (in CDCl$_3$)	59.45	22.22	28.47	22.49	13.87

[a] Spectra of Fig. 5. Two values for C-5 at 400 K show the low- and high-temperature phases.

TABLE VI

^{13}C T_1 of tetra-*n*-pentylammonium bromide (in s)[a]

T (K)	C-1	C-2	C-3	C-4	C-5
308	37.0±2.2	(33.8)[a]	30.6±1.1	(15.4)[a]	1.50±0.04
Isotropization: T_i = 374.0 K, ΔS_i = 97.9 JK^{-1}mol^{-1}					
380	0.077±0.003	0.126±0.004	0.27±0.01	0.74±0.03	1.73±0.05

[a] Resonances of C-2 and C-4 overlap at 308 K, their T_1 were obtained by curve fitting to a bi-exponential function defined by Eq. (5), below, for details see text.

spectra are listed in Table VIII for $(C_6H_{13})_4NBr$, and in Table IX for $(C_6H_{13})_4NI$. The ^{13}C T_1 at temperatures of different phases are listed in Table X for $(C_6H_{13})_4NI$.

Tetra-*n*-heptylammonium Bromide and Iodide

Since the two heptyl salts show great similarity in their thermal behavior,[1] the detailed NMR studies were only carried out for one of them, namely, $(C_7H_{15})_4NI$. For the bromide, only a ^{13}C spectrum, shown in Figure 10 with chemical shifts labeled on the peaks, was measured at room temperature with MAS and high-power decoupling of protons (BILEV) for comparison with the iodide. For $(C_7H_{15})_4NI$ two sets of variable temperature ^{13}C MAS spectra were obtained, one below and one above room-temperature and are shown in Figures 11 and 12, respectively. The chemical shifts of $(C_7H_{15})_4NI$ are listed in Table XI. Solution data are also included in the table. The ^{13}C chemical-shift-anisotropy powder patterns for

TABLE VII

^{13}C T_1 of tetra-*n*-pentylammonium iodide (in s)[a]

T (K)	C-1	C-2	C-3	C-4	C-5
310	39.1±3.8	(36.9)[a]	34.6±2.7	(21.4)[a]	1.18±0.09
Disordering transition: T_d = 404.6 K, ΔS_d = 41.2 JK^{-1}mol^{-1}					
Isotropization: T_i = 412.1 K, ΔS_i = 94.0 JK^{-1}mol^{-1}					
415	0.130±0.004	0.22±0.01	0.43±0.02	1.37±0.04	2.89±0.06

[a] Resonances of C-2 and C-4 overlap at 310 K, their T_1's were obtained by curve fitting to a bi-exponential function defined by Eq. (5), below, for details see text.

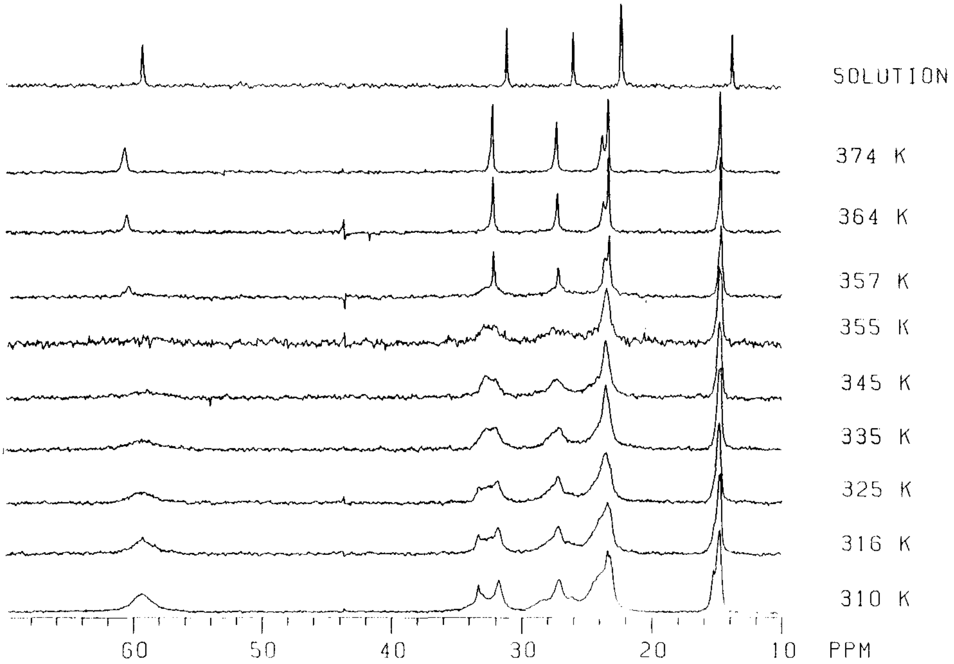

FIGURE 6 ^{13}C CP-MAS NMR spectra of tetra-*n*-hexylammonium bromide. The top spectrum is measured in $CDCl_3$ solution at room temperature. The chemical shifts are listed in Table VIII.

$(C_7H_{15})_4NI$ at some selected temperatures are shown in Figure 13. Finally, the ^{13}C T_1 at temperatures of the different phases are listed in Table XII for $(C_7H_{15})_4NI$.

DISCUSSION

In the discussion, the entropy data obtained from DSC measurements are reviewed first to give an overview of the expected motion and disorder. This is done by using the empirical fusion rules for three types of disordering, namely, positional,[5]

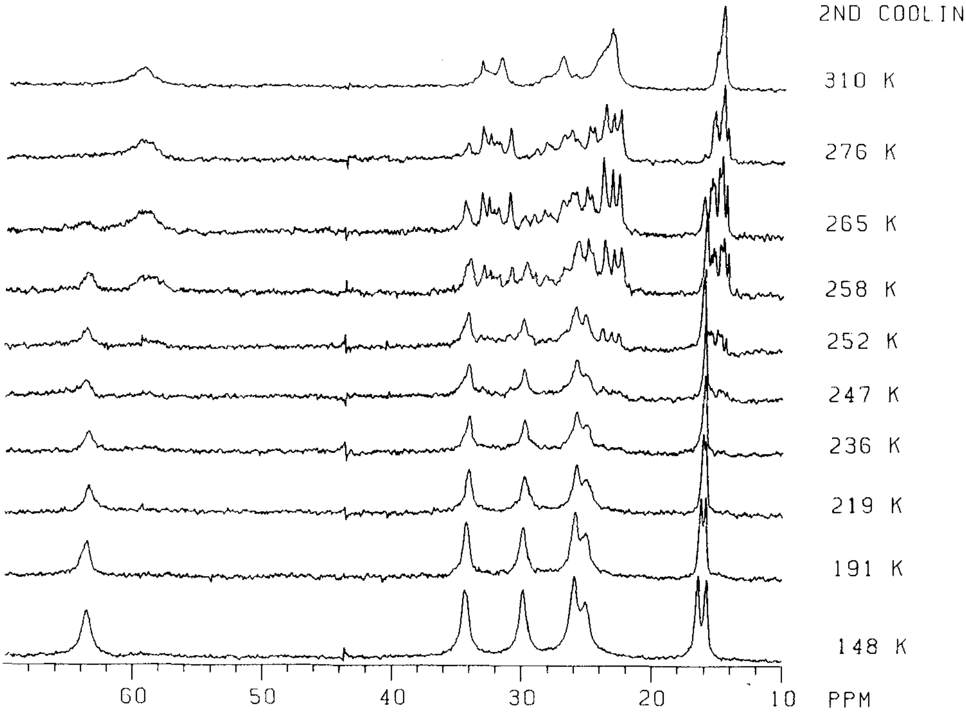

FIGURE 7 ^{13}C CP-MAS NMR spectra of tetra-*n*-hexylammonium bromide obtained on slow cooling (about 10 K/min) from 310 K to 148 K. The chemical shifts of the spectra at 247 and 148 K spectra are listed in Table VIII.

orientational,[6] and conformational,[7–9] that suggest typical entropy changes of 7–14, 20–50, and 7–12 JK^{-1} mol^{-1}, respectively. A detailed analysis on the entropy data on extensive examples using these rules have been demonstrated in paper I of this series.[1]

The positional and orientational motion is molecular size independent, while the conformational motion and disorder is proportional to the number of flexible bonds in the molecule. High resolution ^{13}C NMR is uniquely able to give details on segmental motion, because each individual carbon atoms can be examined. The temperature-dependent ^{13}C chemical shift and spin-lattice relaxation times (T_1) of individual carbon atoms are the most useful pieces of information to understand the conformational motion and disorder in tetra-*n*-alkylammonium salts. In the following, a brief introduction to the relationship between these two NMR parameters and motion will be given first. Next a discussion will be given for each individual salt by analyzing the experimental data of the ^{13}C chemical shifts and the ^{13}C T_1, followed by correlating the NMR results with the entropy changes observed by DSC.

The ^{13}C NMR Chemical Shift

The ^{13}C chemical shift in tetra-n-alkylammonium salts. A systematic chemical shift investigation on the solution ^{13}C chemical shifts of tetra-*n*-alkylammonium

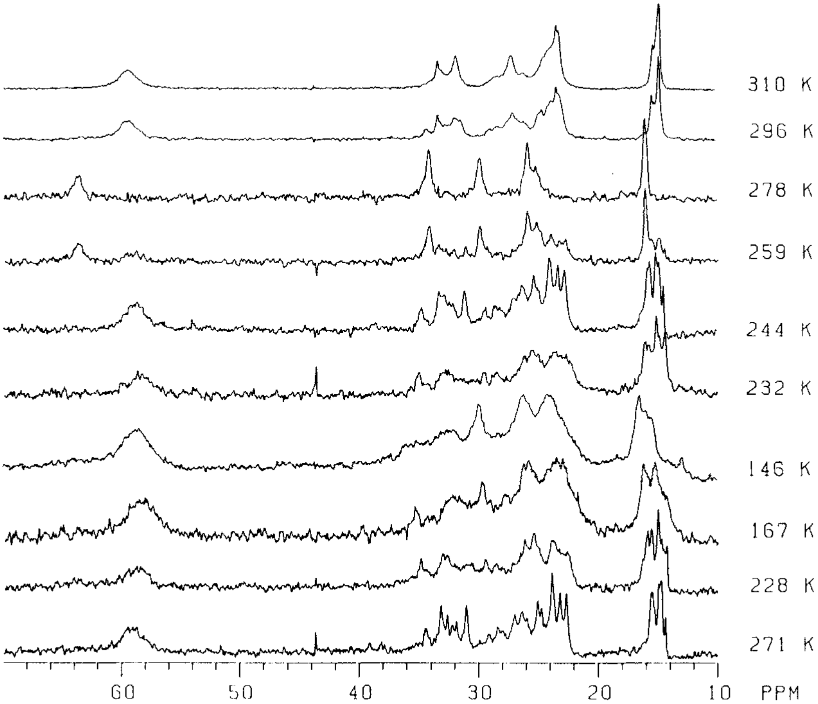

FIGURE 8 ^{13}C CP-MAS NMR spectra of tetra-*n*-hexylammonium bromide obtained on fast cooling from 271 K to 146 K (first four spectra from bottom), followed by heating of the quenched sample (about 10 K/min) from 146 K to 310 K (six spectra shown at the top).

ions with alkyl chain length ranging from 1 to 18 carbon atoms has been carried out using two-dimensional homo-(^1H—^1H) and hetero-nuclear (^1H—^{13}C) chemical shift correlation NMR spectroscopy.[10] It could be shown that the chemical shifts for C-1, C-2, and C-3 can be expressed in terms of α-, β-, and γ-substituent effects arising from both the central N^+ and carbon atoms. For the carbons further removed from the nitrogen atom the empirical additivity rules proposed by Grant and Paul for paraffins apply.[11]

For the high-resolution ^{13}C NMR spectra of solid state tetra-*n*-alkylammonium halides obtained in this research, the signals arising from C-1, C-3, C-*z* (the methyl carbon), and C-*x* (the third carbon from the chain end, i.e., $^{13}CH_2$—CH_2—CH_3) can easily be assigned. These four carbon atoms have unique chemical shift values, i.e., the chemical shift variation of these four carbon atoms, over the entire temperature range is less than the chemical shift difference between them and any other carbons. The signal of C-2 overlaps, in the vicinity of room temperature, partially with that of C-*y* (the methylene carbon connected to the methyl group) as shown in Figures 4–6 and 9–11. The partly overlapping signals of C-2 and C-*y* appear at 24.4–25.3 ppm. Distinction between C-2 and C-*y* can be made through their relaxation times. The carbon atom closer to the end of the chain has the greater mobility. Furthermore, the more rigid C-2 shows usually a broader and weaker signal, therefore, C-2 normally appears as a shoulder on the sharper,

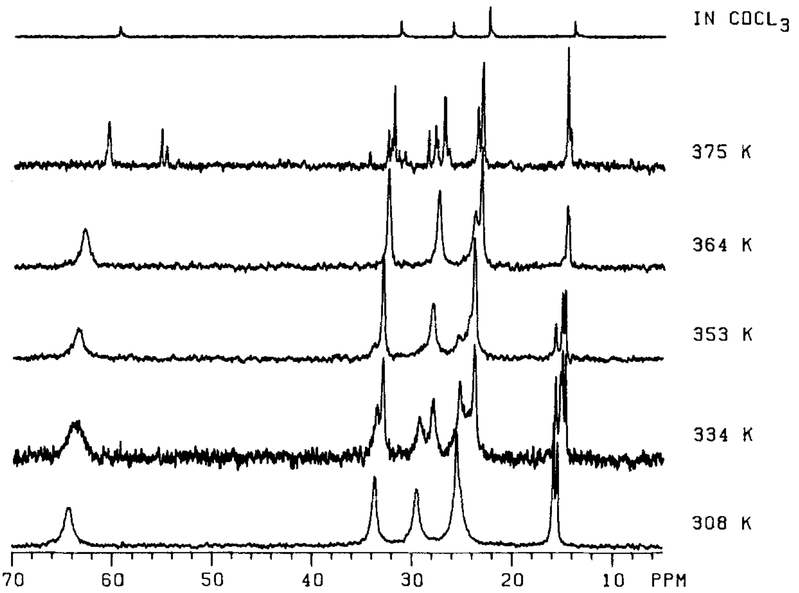

FIGURE 9 ^{13}C CP-MAS NMR spectra of tetra-*n*-hexylammonium iodide. The top spectrum is measured in $CDCl_3$ solution at room temperature. The chemical shifts are listed in Table IX.

TABLE VIII

^{13}C chemical shifts of tetra-*n*-hexylammonium bromide as a function of temperature (in ppm relative to TMS)

T (K)	C-1	C-2	C-3	C-4	C-5	C-6
148[a]	63.56	25.07	29.82	34.31	25.94	16.43/15.79
247[a]	63.43	24.98	29.79	34.05	25.78	15.97
Disordering transitions at: 148, 167, 196, and 305 K, with entropy changes of: 8.1, 1.2, 17.5, and 22.0 $JK^{-1}mol^{-1}$, respectively						
310[a]	59.32	24.33	27.06	33.22/31.71	23.30	15.23/14.72
Disordering transition: T_{ds} = 315 K, ΔS_{ds} = 38 $JK^{-1}mol^{-1}$ Isotropization: T_i = 374.9 K, ΔS_i = 42.6 $JK^{-1}mol^{-1}$						
374[b]	60.46	23.59	27.13	32.07	23.14	14.57
Solut.[b]	59.33	22.41	26.10	31.25	22.41	13.93

[a] Spectra of Fig. 7. Two values are given for double peaks arising form the same carbon atom.

[b] Spectra of Fig. 8.

TABLE IX

^{13}C chemical shifts of tetra-*n*-hexylammonium iodide as a function of temperature (in ppm relative to TMS)[a]

T (K)	C-1	C-2	C-3	C-4	C-5	C-6
308	64.41	25.00	29.47	33.66	25.52	15.83/15.45
Disordering transitions: T_{d1} = 345.1 K, ΔS_{d1} = 83.3 $JK^{-1}mol^{-1}$ T_{d2} = 352.3 K, ΔS_{d2} = 16.2 $JK^{-1}mol^{-1}$						
364	62.93	23.80	27.36	32.40	23.14	14.60/14.46
Isotropization: T_i = 378.7 K, ΔS_i = 43.9 $JK^{-1}mol^{-1}$						
380	60.48	23.58	26.60	31.87	23.50	14.55
Solut.	59.29	22.41	26.04	31.21	22.41	13.93

[a] Spectra of Fig. 9. Two values are for the two peaks arising from the methyl carbon, see Fig. 8.

TABLE X

^{13}C T_1 of tetra-*n*-hexylammonium iodide (in s)[a]

T (K)	C-1	C-2	C-3	C-4	C-5	C-6
308	43.0	(39.0)	36.0	29.1	(14.5)	2.5
322	36.0	(34.1)	32.5	20.2	(11.5)	2.3
Disordering transitions: T_{d1} = 345.1 K, ΔS_{d1} = 83.3 $JK^{-1}mol^{-1}$ T_{d2} = 352.3 K, ΔS_{d2} = 16.2 $JK^{-1}mol^{-1}$						
358	0.29	0.43	0.87	1.78	2.44	3.46
Isotropization: T_i = 378.7 K, ΔS_i = 43.9 $JK^{-1}mol^{-1}$						
380	0.094	0.108	0.32	0.98	1.95	3.61
Solut.	0.25	0.30	0.50	1.38	1.75	2.75

[a] Data in parentheses are for C-2 and C-5, since their resonances overlap, their T_1 were obtained by curve fitting to Eq. (5). The solution data are taken from Ref. 4.

stronger signal of C-*y* (see, for example, Figure 9 for $(C_6H_{13})_4NI$ at 308 K). As the temperature is increased, better resolutions can be realized because the increased conformational motion of C-*y* causes a much larger up-field shifting for the C-*y* signal.

A solid-state ^{13}C MAS NMR spectrum becomes more and more like that of the solution as the temperature increases, i.e., signals become sharp and well separated. The manner and amplitude of chemical-shift changes during phase transitions (or as a function of temperature) can be interpreted in terms of conformational and orientational motion and disordering of the cation.

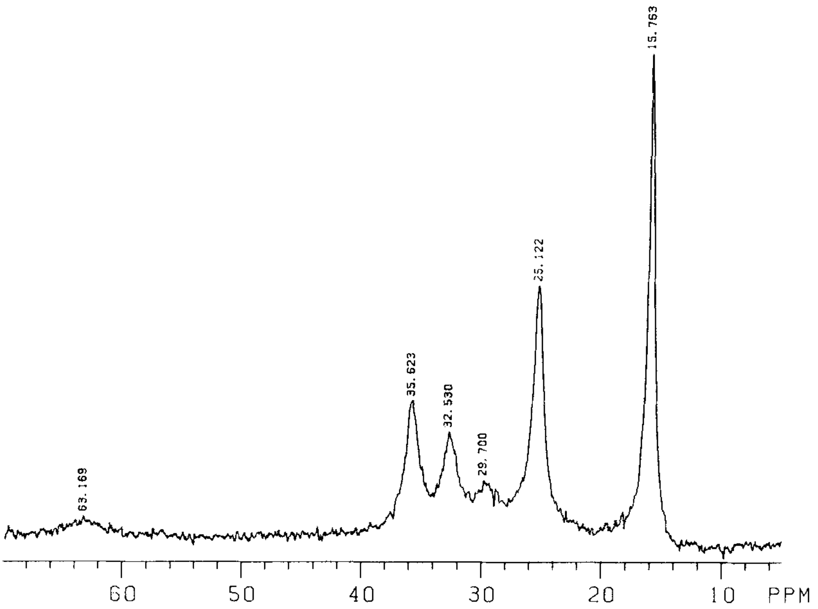

FIGURE 10 Room-temperature ^{13}C NMR (50.3 MHz) spectra of tetra-*n*-heptylammonium bromide obtained with magic angle spinning and BILEV decoupling. The chemical shifts are labeled on each peak.

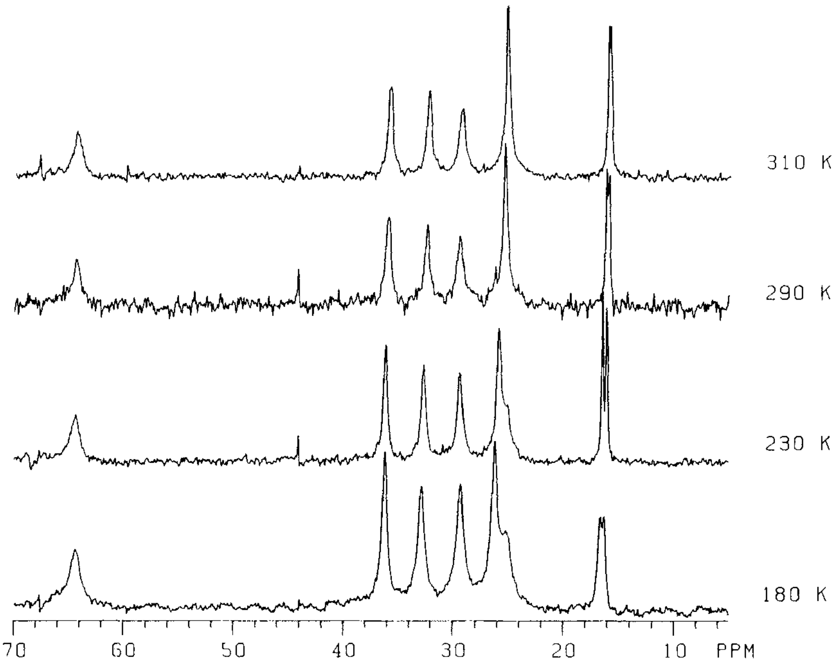

FIGURE 11 Low temperature ^{13}C CP-MAS NMR spectra of tetra-*n*-heptylammonium iodide. The chemical shifts are listed in Table XI.

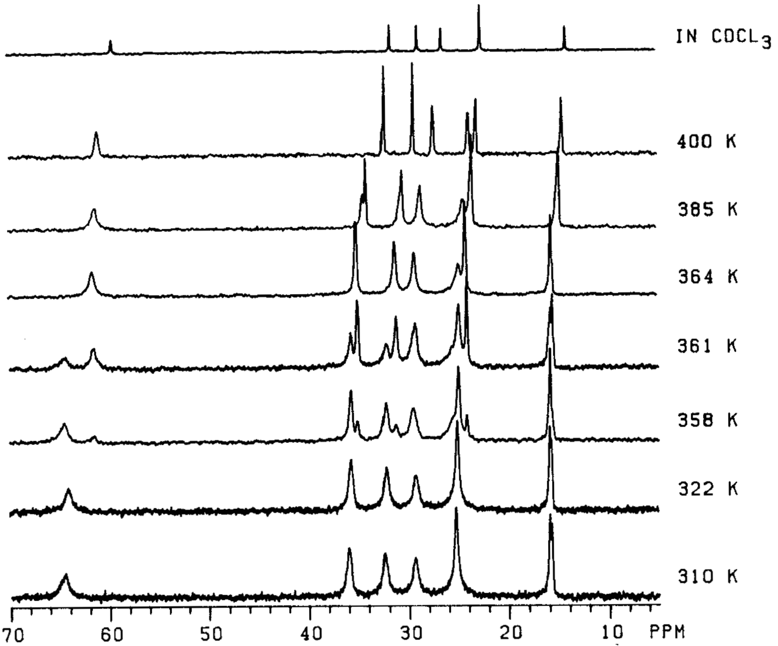

FIGURE 12 ^{13}C NMR spectra of tetra-*n*-heptylammonium iodide obtained with magic angle spinning of BILEV decoupling. The top spectrum is measured in $CDCl_3$ solution at room temperature. The chemical shifts are listed in Table XI.

The γ-gauche effect. Even in the solid state, the changes in intramolecular conformations are the most important influence on the ^{13}C chemical shift (δ values). The intermolecular effect on the ^{13}C δ values is of secondary importance. Specifically, δ is influenced by substituents attached to the observed carbon in the α-, β- and γ-positions, causing so-called α-, β- and γ-substituent effects. The first two effects are constant (independent of chain conformation) as long as the chemical structure of the molecule is fixed. The γ-substituent effect, however, has a conformational contribution[12,13] because the observed carbon, ^{o}C, and its γ-substituent, $^{\gamma}$C, are separated ($^{o}CH_2—CH_2—CH_2—^{\gamma}CH_2$) such that their mutual distance and orientation depend on the conformation of the central bond (or rotational isomeric state). For a ^{13}C to be more shielded by a γ-substituent, the ^{o}C and $^{\gamma}$C must be in a gauche arrangement, and the effect of γ-gauche shielding can be evaluated to be $\gamma_{C—C} = -5.2$ ppm.[12] In the melt or solution between 250 and 400 K, the rotating C—C bonds are expected to have a population of approximately 40% gauche conformations, a value adopted by Flory for the melt of polyethylene.[14] One would thus expect that after a transition from a fully ordered trans bond to 40% of gauche, the δ of the corresponding ^{13}C to decrease (be more shielded) by:

$$\Delta\delta = 2 \times (0.4) \times (-5.2) \text{ ppm} = -4.16 \text{ ppm}$$

The factor of two accounts for a possible γ-substituent on both sides of the observed carbon. If only one of the two γ-substituents has become gauche to ^{o}C, the Δδ

TABLE XI

^{13}C chemical shift of tetra-*n*-hexylammonium iodide as a function of temperature (in ppm relative to TMS)

T (K)	C-1	C-2	C-3	C-4	C-5	C-6	C-7
180^a	64.37	25.21	29.29	32.83	36.18	26.22	16.61/16.26^c
230^a	64.31	25.05	29.33	32.62	36.09	25.84	16.41/16.01^c
290^a	64.27	25.14	29.33	32.28	35.81	25.14	16.02/15.82^c
310^{a,b}	64.19	25.17	29.35	32.27	35.84	25.17	15.93/15.74^c
322^b	64.18	25.04	29.19	32.20	35.68	25.04	15.85
Disordering transition: T_{d1} = 355.4 K, ΔS_{d1} = 26.1 JK^{-1}mol^{-1}							
364^b	61.51	24.78	29.20	31.15	34.96	23.44	15.58
385^b	61.22	24.31	28.58	30.42	33.97/34.29^a	23.44	14.77
Disordering transition: T_{d2} = 391.0 K, ΔS_{d2} = 6.2 JK^{-1}mol^{-1} Isotropization: T_i = 398.7 K, ΔS_i = 97.9 JK^{-1}mol^{-1}							
400^b	61.04	23.84	27.36	29.32	32.24	23.02	14.56
Solut.^{b}	59.38	22.48	26.36	28.80	31.54	22.48	14.06

a Spectra of Fig. 11,
b Spectra of Fig. 12,
c Two values are for the two peaks arising from the same carbon atom.

would naturally be −2.08 ppm. Similarly, if neither of the γ-substitutents has changed its spatial relationship with respect to °C, Δδ is zero. As temperature is increased, the δ of a ^{13}C in the linear paraffinic chains may thus change by values close to 0, −2, or −4 ppm due to conformational disordering only. Intermediate values for Δδ are also possible, since the concentration of gauche conformation is variable with temperature.

It must be noted that in tetra-*n*-alkylammonium cations, the γ-gauche effects are normally observed in the alkyl chains with sufficient length ($n \geqslant 6$). For smaller cations, the chemical shift changes can not be interpreted purely by the γ-gauche effect. The reasons for the failure of the observation of the γ-gauche effect may be the intermolecular interaction, which involves changes in the anion placement, comparable to, or more important than the conformation-dependent γ-gauche effect. It may also be possible that the change in equilibrium ratio of trans-to-gauche is less than the longer-chain cations that approach the paraffin structure.

Intermolecular influences on the ^{13}C chemical shift. Complications in the chemical shift arise in small molecules that have an a priori possibility of motion of the molecule as a whole. In this case the packing (intermolecular interaction) can be changing when motion begins. The influence of changes in packing on the ^{13}C

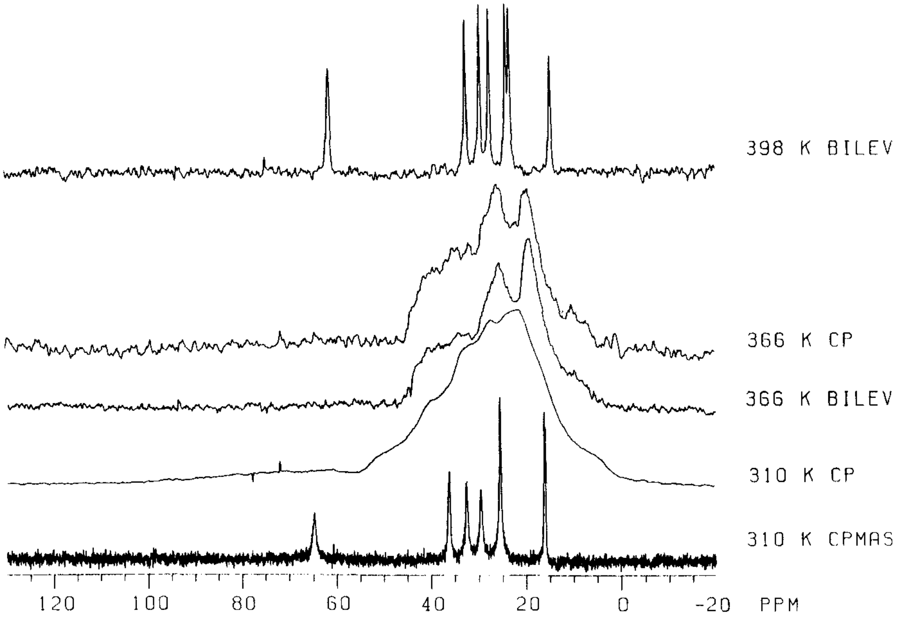

FIGURE 13 ^{13}C NMR powder patterns of tetra-*n*-heptylammonium iodide. CP stands for cross-polarization and BILEV stands for Bloch decay. The bottom is the CP-MAS spectrum at 310 K to show the isotropic resonance positions.

TABLE XII

^{13}C T_1 of tetra-*n*-heptylammonium iodide (in s)[a]

T (K)	C-1	C-2	C-3	C-4	C-5	C-6	C-7
310	33.5	(33.4)	33.3	22.3	14.4	(7.00)	2.31
322	28.0	(26.0)	24.0	15.4	10.4	(5.10)	3.10
Disordering transition: T_{d1} = 355.4 K, ΔS_{d1} = 26.1 JK^{-1}mol^{-1} Disordering transition: T_{d2} = 391.0 K, ΔS_{d2} = 6.2 JK^{-1}mol^{-1}							
395	0.25	0.35	0.37	0.79	1.06	2.15	4.29
Isotropization: T_i = 398.7 K, ΔS_i = 97.9 JK^{-1}mol^{-1}							
405	0.09	0.16	0.39	0.73	1.44	2.14	4.55

[a] Data in parentheses are for C-2 and C-6, since their resonances overlap, their T_1 were obtained by curve fitting to Eq. (5).

chemical shifts is perhaps more important in the ionic crystals of this research than in non-ionic organic crystals since the electron shielding of the ^{13}C nucleus determines the value of ^{13}C chemical shift. Moreover, the change of packing is often coupled with changes in conformation of flexible bonds, and sometimes even with changes in valence angle (which occurs in Et$_4$NI, proven by X-ray diffraction[2,15]), making the ^{13}C chemical shift more difficult to predict in these cases. For tetra-*n*-alkylammonium halides, these difficulties will be overcome by considering also X-ray structure analysis as a function of temperature.[16,17]

Interpretation of ^{13}C Spin-lattice Relaxation Times

When the signals are well resolved, it is possible to measure the ^{13}C T_1. The T_1 data are most useful to evaluate the mobility, as illustrated in the following. It was found by Lyerla and Levy[18] that for large molecules with a number of reorientational modes the relaxation data can be analyzed semiquantitatively to obtain effective correlation times, τ^{eff}, for each carbon via:

$$\frac{1}{nT_{1C}} = \frac{\gamma_C^2\gamma_H^2\hbar^2}{40\,\pi^2 r^6}\left[\frac{\tau}{1 + (\omega_H - \omega_C)\tau^2} + \frac{3\tau}{1 + \omega_C^2\tau^2} + \frac{6\tau}{1 + (\omega_H + \omega_C)^2\tau^2}\right] \tag{1}$$

where γ_H and γ_C are the magnetogyric ratios of the ^1H and ^{13}C nuclei, respectively. the constants, ω_H and ω_C are the resonant frequencies in radians/s for ^1H and ^{13}C, respectively ($2\pi \times 200$ MHz and $2\pi \times 50.3$ MHz in this work). The distance between the interacting nuclei ^{13}C and ^1H, r, can be taken as 0.109 nm in methylene and methyl groups. The integer n is the number of protons attached to the carbon, for a methylene group $n = 2$ and for a methyl group $n = 3$. The correlation time τ is then determined by the measured T_1. The value of T_1 given by Equation (1) shows a minimum at $\omega_C\tau = 0.793$, or $\tau = 2.52$ ns.

In tetra-*n*-alkylammonium salts of intermediate alkyl chain length, below the melting transition, it was found that: (1) T_1 increases progressively from the chain end (the methyl group) to C-1; (2) T_1 of each carbon decreases as a function of temperature (except for the methyl carbon). These observations suggest that the correlation time of the methylene carbons are at the long-time side of the T_1 minimum (except for the methyl carbon). On the other hand, in the melt or in the plastic crystalline phase, the trends in T_1 as a function of position of carbon atoms and in temperature dependence of each carbon are exactly reversed, indicating that the correlation times are now at the short-time side of the T_1 minimum.

Next, we separate the motion of the C—H vector in the alkyl chains in terms of orientational motion of the cation as a whole (the alkyl chains are considered as rigid rods) with an average rate τ_o^{-1} and an internal conformational motion about the individual C—C bonds in the alkyl chains with rate τ_i^{-1}. The expression for the rate of motions of the jth carbon in the side chain, $(\tau^j)^{-1}$, is then the sum of the two rates[18]:

$$\frac{1}{\tau^j} = \frac{1}{\tau_o^j} + \frac{1}{\tau_i^j} \tag{2}$$

The differential rate between the lth and mth carbons is:

$$\frac{1}{[\tau(l, m)]} = \frac{1}{\tau^l} - \frac{1}{\tau^m} \tag{3}$$

Substituting Equation (2) into Equation (3), and realizing that $1/\tau_o^l = 1/\tau_o^m$, Equation (3) becomes:

$$\frac{1}{[\tau(l, m)]} = \frac{1}{\tau_i^l} - \frac{1}{\tau_i^m} \tag{4}$$

The quantity $1/\tau(l, m)$ should involve only internal correlation times and represents the difference in rates of the conformational motion between the lth and mth carbons.

Small differential rates have been found for C-1 and C-2 in tetra-*n*-propylammonium halides studied in the second paper of this series of publication,[2] and it will be seen that small differential rates are generally found for the inner-most bonds (close to the nitrogen), indicating slow conformational motion, very much in line with the calorimetric result that two of the CH_2-groups remain conformationally immobile even in the melts.

Tetra-*n*-butylammonium Bromide and Iodide

The transition parameters were observed in the DSC experiments and discussed before.[1] The values are listed in Tables I and II. Based on the entropy data, it could be deduced, using the empirical fusion rules, that in the iodide the orientational disordering of the cation and conformational disordering for about one bond per alkyl chain occur together at the low-temperature transition (394.0 K), while complete positional disordering takes place without major additional conformational disordering on isotropization (420.6 K). For the bromide, in contrast, the low-temperature transition (367.0 K) can only be linked to conformational disordering about one bond per alkyl chain. Partial orientational disordering seems then to occur gradually between the disordering and the isotropization temperature (393.9 K), helped by a minor transition at 379.2 K. This conclusion was based on the observation that the entropy change at isotropization is only about 16 JK^{-1} mol^{-1} (after subtracting 21.3 JK^{-1} mol^{-1} for the positional disordering of a $(C_4H_9)_4N^+$ ion obtained from $(C_4H_9)_4NI$). This is lower than the typical 20–50 JK^{-1} mol^{-1} expected for orientational disordering, or the average value of 44.9 JK^{-1} mol^{-1} for the four previously analyzed low-homolog tetraethyl and tetra-*n*-propyl compounds,[1,2] or the value of about 33 JK^{-1} mol^{-1} for $(C_4H_9)_4NI$, deduced from Table II. Because of this complication of the bromide, the discussions of the NMR results will be given first for the "well-behaved" iodide salt.

Iodide. The state of orientational motion and disorder of the cation can be shown by several solid state ^{13}C NMR methods. The ^{13}C NMR spectra obtained under MAS conditions below T_d (see Figure 2) show multiple lines for the methyl carbon (C-4). The resonance of C-4 can be decomposed into three peaks at 14.40, 15.29 and 15.53 ppm, with integral intensity ratios of 2:1:1. Since the separation between the most upfield and downfield peaks is too small (only 1.1 ppm) to account for the γ-gauche effect (about 2 ppm), we surmise that the multiplicity of the resonance of the C-4 carbons has an intermolecular reason, such as different distances between C-4 and the iodine ion, as was observed for the case of tetra-*n*-

propylammonium iodide, discussed in paper II of this series.[2] The area ratio of 2:1:1 implies that only two of the four C-4 atoms have the same environment in the crystal. A detailed crystal structure from single crystal X-ray data is needed to verify this interpretation.[17] As the temperature is increased to T_d, the spectra at 395 and 402 K in Figure 2 show clearly that another peak (14.79 ppm) at the average position of the previous peaks becomes stronger and finally dominates at 409 K. The appearance of the new peak is due to orientational motion of the cation as a whole, which renders all four methyl groups equivalent.

The orientational motion of the cation as a whole is also indicated by the changes in the other carbon signals of Figure 2. The changes in chemical shift occur mainly during the disordering transition T_d (Table II). The differences in chemical shift between 310 and 409 K are 0.61, 0.83, 0.85 ppm for C-1, C-2, and C-3, respectively. The outer carbons are affected more, which is in line with changes in intermolecular interaction arising from orientational motion and disordering.

The most decisive information on the orientational motion of the cation as a whole is given by the variable temperature ^{13}C powder pattern shown in Figure 3. Below 394.0 K, the resonance of C-1 yields a typically broad anisotropic pattern, indicative of the absence of motion. Above 394.0 K, the C-1 resonance is narrowed (see spectrum at 400 K). The narrowing of C-1 signal is due to orientational motion which is the only allowed freedom for C-1. Below 394.0 K, the more closely-spaced resonances of C-2, C-3, and C-4 feature also broadening to a degree that they are fused to a single peak at about 25 ppm. The orientational motion and superimposed conformational motion of the bond C2—C3 (analyzed in the following) at 400 K results in a much better resolution so that the three peaks can now be distinguished easily.

The ^{13}C spin-lattice relaxation times, listed in Table III, can be used to evaluate the mobility of the orientational motion and disorder discussed above. Below the transition temperature, T_1 of C-1, C-2, and C-3 are of the same order of magnitude, between 40 and 60 s, corresponding to a motional correlation time τ_C between 2.9 and 4.3 μs [calculated from Equation (1)]. This is much slower than what is found in plastic crystals (typically, orientational motion of 5 ns at the crystal-to-plastic crystal phase transition and 2 ps at isotropization).[19] The relaxation time for C-4 is very short (1.7 s) because of the fast rotation of the methyl groups about their C_3-axes. As the temperature is increased to 408 K, τ_C calculated from the data in Table III with Equation (1) for C-1 and C-2 is 0.54 and 0.32 ns, respectively, both typical for plastic crystals.

Of particular interest is the conformational motion and disorder initiated at T_d. In the previous paper[2] we have shown that (1) N—C1 and C1—C2 are for steric reasons practically rigid, even in solution, (2) the methyl rotation starts at very low temperature and does not change the overall molecular conformation. Therefore, the conformational disordering in a tetra-*n*-butyl cation is expected to be introduced only through the bond between C-2 and C-3.

Using Equations (1)–(4), the conformational motion in C—C single bonds can be proven by the differential rates of motion between adjacent bonded carbon atoms.[18] The larger the difference in $1/\tau$, the faster is the motion about the bond. At 329 K, the correlation times, τ, calculated from the measured T_1 listed in Table

III, for C-1 to C-4 are 3.78 μs, 4.33 μs, 3.05 μs, and 19.9 ps, respectively. The small differences between the correlation times of C-1 and C-2 and between C-2 and C-3 indicate that the C1—C2 and C2—C3 bonds are rigid. As the temperature is increased to 408 K, the calculated values for τ are 0.54 ns, 0.32 ns, 92 ps and 22.4 ps for C-1 to C-4, respectively. The values of τ for C-1 and C-2 are still very close, but the difference between C-2 and C-3 is much larger than that between C-1 and C-2, indicating the presence of conformational motion about the bond between C-2 and C-3. The overall decrease in T_1 of all three inner carbons (C-1 to C-3) is due to the orientational motion of the cation as a whole. Similar T_1 values for C-1 and C-2 can even be found in the solution,[4] as represented in Table III, indicating that the bond between C-1 and C-2 is in all states prohibited from rotation.

Bromide. At room temperature the ^{13}C CP-MAS NMR spectrum, shown in Figure 1 at 308 K, is almost the same as that for the iodide. The differences between the two butyl compounds in the chemical shifts for all the carbon atoms are very small (within 0.3 ppm, see the results in Tables I and II). The methyl carbon atoms (C-4) in both salts show the same three-line pattern with the same intensity ratio of 2:1:1. These similarities suggest that the bromide salt forms as well-ordered crystals as the iodide.

The conformational motion and disorder can only be inferred from the relaxation time measurements, since the chemical shifts for all carbon atoms change little in going through the disordering transitions. The spin-lattice relaxation times for C-2 and C-3 in the mesophase at 384 K are 10.0 and 1.51 s, respectively. This large difference in T_1 between C-2 and C-3 proves that the bond C2—C3 is conformationally mobile above T_d. These T_1 values correspond to correlation times of 0.72 and 0.11 μs, indicating a motion that is slower by two orders of magnitude than typically found in a plastic crystal. Thus, the mesophase formed at T_d = 367.0 K must be a condis state without orientational motion. The condis state of $(C_4H_9)_4NBr$ (as well as all other compounds studied in this research) is spectroscopically unique, because one can use either CP-MAS (designed for rigid carbon atoms) or BILEV (routinely used for solution ^{13}C NMR) to obtain a ^{13}C spectrum with good signal-to-noise ratio. The reason is that in the condis state the mobility is intermediate between that of a rigid molecule in the crystalline state and that of tumbling molecules in the melt (or solution). Signals from the carbon atoms in conformationally mobile chains of liquid crystals, such as in OOBPD,[20] and plastic crystals (such as in $(C_4H_9)_4NI$) can only be detected with the BILEV method, therefore, have a much higher mobility than the molecules in their condis state in which both orientational and positional order remain.

Information on the gradual orientational disordering can be obtained from the spectra in Figure 1. The spectral lines for all carbon atoms show continuous broadening from 373 to 384 K. Similar line broadening was found for tetra-*n*-propylammonium iodide below its crystal-to-plastic transition temperature.[2] This line broadening can be attributed to the fact that the orientational motion (of the cation as a whole) has attained a relatively large amplitude so that the intermolecular interactions are changed. This large-amplitude orientational motion is then also most probably responsible for the deficit of the orientational entropy observed on isotropization. Final confirmation is expected from a detailed analysis of the heat capacity, presently in progress. The orientational motion detected by the line broadening in ^{13}C NMR spectrum can, however, only be a restricted motion, since the C-4 (methyl) resonances consist of at least two lines (Figure 1), indicating two distinguishable methyl group placements in the crystal. If the orientational motion were the same as in the iodide, i.e., isotropic or random, the C-4 resonances should have undergone coalescence into a single, sharp peak.

At 392 K, the NMR spectrum is already largely that of the melt (395 K). The remaining differences in chemical shifts between the solution and the melt spectra, shown also in Figure 1, are due to the solvent effect, i.e., differences in intermolecular interactions, if one assumes that the mobility is the same in both cases.

From this discussion, it can thus be concluded that tetra-*n*-butylammonium bromide and iodide: (1) form well ordered crystals that possess practically only vibrational motion below the mesophase transitions, (2) between the mesophase transition temperatures and the isotropization temperatures, the cations in the iodide salt form a plastic crystal with additional conformational motion and disorder about the bond C2—C3, while the bonds N—C1 and C1—C2 remain rigid. The cations of bromide salt are similarly conformationally disordered, but remain largely orientationally ordered with gradually increasing orientational mobility as the temperature is increased; (3) the N—C1 and C1—C2-bonds remain in a fixed conformation in both salts even in the liquid state, therefore, the maximum degree of conformational disorder has been realized already well below isotropization.

Tetra-*n*-pentylammonium Bromide and Iodide

Bromide. There is only one phase transition observed for the bromide (374.0 K) with an entropy change of 97.9 JK^{-1} mol^{-1}. Since the transition is identified as the melting, the entropy change consists of all three disorder contributions. If one subtracts the positional and orientational contributions from the observed entropy, one obtains 25–39 JK^{-1} mol^{-1} for conformational disordering. This conformational disorder can be attributed to 4 bonds becoming disordered. Based on the analysis of the shorter chain homologs, the tetra-*n*-pentylammonium cation should have, however, 8 single bonds to be disorderable, namely, C2—C3 and C3—C4. The questions are thus (1) which four bonds contribute to the entropy change? (2) what is the behavior of the other four bonds that do not contribute to the transition entropy, are they already disordered at the lower observation temperature or do they remain ordered even in the melt?

Figure 4 reveals the transition at 373 K through chemical shift changes (see also Table IV). In going through the phase transition, except for C-1, the chemical shift changes between 308 and 387 K are close to 1.5 ppm. The phase transition is also obvious from the drastic decrease in T_1 for all carbon atoms but C-5, as shown in Table VI. Since conformational motion about the bond between C-1 and C-2 is not possible, the sharp decrease in T_1 of C-1 and C-2 between 308 K and 380 K must be due to the orientational and translational motion. The relaxation times for C-2 and C-4 at 308 K can not be directly measured since their signals are overlapping, but since both C-1 and C-3 have large T_1 values (37.0 and 30.6 s, respectively), the T_1 of C-2 is expected to be long, too, between 37 and 30 s, permitting the assignment given in Table VI. Thus, the bond between C-2 and C-3 is considered to be conformationally rigid at 308 K. As the temperature is increased to 380 K (above the transition), the signals of C-2 is well separated from that of C-4, as shown in Figure 4, and it is possible to measure T_1 of C-2 and C-4 directly. The difference in T_1 between C-2 and C-3 has become larger than that between C-1 and C-2. Therefore, the bonds of C2—C3 can be assumed to contribute most to the entropy change of 25–39 JK^{-1} mol^{-1} at the transition. If the bonds between C-3 and C-4 contribute little to the entropy change at the transition, one must assume them to have considerable motion and be disordered already below the transition, since they are certainly conformationally mobile above the transition (as seen from T_1 of C-3 and C-4 at 380 K).

Supporting evidence for these assumptions is as follows: The relaxation time of C-4 at 308 K could not be obtained directly from measurement due to the overlapping between signals of C-4 and C-2, it was, however, possible to carry out a reliable estimation by knowing that: (1) T_1 of C-2 is between that of C-1 and C-3, i.e. between 37.0 and 30.6 s, (2) the relationship between the measured overlapping signal intensity, $I(t)$, and the variable delay, t, could be measured using the progressive saturation method and fitted to the following equation:

$$I(t) = I_0[(A - e^{-t/T_1(C2)}) + (B - e^{-t/T_1(C4)})] \qquad (5)$$

in which I_0 is $I(t)$ at $t = \infty$, A and B are two constants (both are close to unity), T_1(C2) and T_1(C4) are T_1 of C-2 and C-4, respectively. The constants, I_0, A, B, T_1(C2) and T_1(C4) are treated as adjustable parameters with constraints as stated above. As shown in Table VI, the large difference in T_1 between C-3 and C-4 at 308 K agrees with the above made suggestion that C3—C4 is in motion and disordered already at 308 K. Again, a full support of the gradual disordering about C3—C4 is expected from a detailed heat capacity analysis, presently in progress.

Iodide. The total entropy change of the two observed phase transitions of the iodide is 135.2 JK^{-1} mol^{-1},[1] which suffices to account for all disordering to occur within these closely spaced transitions. The conformational disordering applies to the 8 bonds, (C3—C4) and (C2—C3). The low-temperature transition at 404.6 K has an entropy change of 41.2 JK^{-1} mol^{-1} and was assigned to the disordering of four equivalent bonds to a condis crystal.

It is difficult to obtain a ^{13}C spectrum for this condis phase in the slow NMR experiment. The sample undergoes a complete transition to the melt within the time of taking an NMR spectrum. The spectra of the room-temperature phase crystal (305, 362 K and 384 K) of Figure 5 show that the signals for C-2 and C-4 become more resolved as the temperature is increased because of an up-field shifting of the C-4 resonance, while all other resonances remain practically unchanged. This change indicates that the conformational motion in the chain has already started gradually below the transition temperature. Since this motion excited does not lead to a major increase in entropy, the motion should not substantially disturb the crystal symmetry.

The biggest change in the spectra shown in Figure 5 can be seen at the phase transition (T_d = 404.6 K). The two distinct lines arising from the methyl carbons at 400 K are representatives of the room-temperature phase (15.52 ppm peak) and the condis phase (14.71 ppm peak). The other carbons show only single lines and their chemical shifts differ only slightly from those measured at 305 K. As the temperature is increased to 415 K (the melt), the room-temperature phase disappears, and the methyl group shows one peak only at 14.62 ppm. The C-2 and C-4 signals are clearly separated. Chemical shift changes for all carbon atoms from 400 to 415 K, listed in Table V, are due to the combined effects of all three types of disordering during isotropization.

The ^{13}C, T_1 data listed in Table VII for tetra-*n*-pentylammonium iodide can be interpreted in the same way as for the bromide. In the room-temperature phase of the iodide, the bond between C-3 and C-4 is, however, more rigid than in the bromide (as can be seen from the smaller differences in the T_1's between C-3 and C-4 in the iodide). Above the melting point, the T_1 for all carbons increases from C-1 to C-5. The differences in T_1 between two directly bonded carbon atoms also increases as one approaches the chain end, indicating the increasing conformational mobility at the chain end. The small difference in T_1 between C-1 and C-2 is perhaps due to the motion in C2—C3.

Tetra-*n*-hexylammonium Bromide and Iodide

The thermal behavior of the bromide was shown in the first paper of this series of publication[1] to be more complicated than that of the iodide. The bromide has five disordering transitions before isotropization at 375 K (see Table VIII). The transitions with small entropy changes ($\leq$20 JK^{-1} mol^{-1}), are most likely crystal structure changes occurring without major increases in motion (to be verified by X-ray diffraction). These transitions of small entropies may, however, cause considerable changes in the chemical shift of ^{13}C NMR and make it difficult to investigate the, for us, more interesting conformational motion and disorder. For this reason, we will discuss the simpler case of the iodide first.

Iodide. Below the isotropization temperature (378.7 K) the combined entropy change for two closely spaced disordering transitions (345.1 and 352.3 K) is 99.5 JK^{-1} mol^{-1}, which is sufficient to account for approximately three bonds per alkyl chain (or a total of 12 bonds) to become disordered.[1] Therefore, the sample should be a well-ordered crystalline phase at room temperature, and a condis phase with maximum amount of conformational disorder above 352 K that retains positional and orientational order. The isotropization transition (at 378.7 K) has the expected entropy change of 43.9 JK^{-1} mol^{-1} for the orientational and positional disordering.

The room-temperature phase ^{13}C CP-MAS spectrum, plotted in Figure 9, shows two lines from the methyl group, a pattern similar to that found in tetra-*n*-butylammonium iodide, suggesting that the cations are orientationally ordered. The relaxation times listed in Table X show that below the disordering transition all the carbon atoms have long, comparable values for T_1, suggesting that the chains are conformationally rigid. The decrease of T_1 for C-4 and C-5 is probably due to the methyl rotation.

The spectra obtained at 334, 353 and 364 K in Figure 9 show the progressive formation of the condis phase and disappearance of the room-temperature crystalline phase. In the condis phase of 358 K, the relaxation times for all carbons atoms have decreased to values similar to that in the melt or in solution. From Table X, the mobility about each bond can be assessed from the differences in T_1 between directly bonded carbon atoms. At 358 K all bonds, except for C1—C2, have considerable motion which increases when approaching the chain end.

The changes in chemical shift between room temperature and condis phase can for this chain length also be used to document conformational disorder and motion. From Table IX, the chemical shift differences between 308 and 364 K are sufficiently close to 2 ppm, to suggest that one γ-substituents of each carbon atom has substantially increased in its gauche content. The changes in the chemical shifts of C-1, $\Delta\delta$(C-1), is due to the conformational disorder in the bond C2—C3, and similarly, $\Delta\delta$(C-2) due to C3—C4, $\Delta\delta$(C-3) due to C4—C5, $\Delta\delta$(C-4) due to C2—C3, $\Delta\delta$(C-5) due to C3—C4, and $\Delta\delta$(C-6) due to C4—C5. This indicates that the chemical shift changes for all six carbon atoms are due to three bonds only, i.e., C2—C3, C3—C4, and C4—C5, while the remaining three bonds, N—C1, C1—C2, and C5—C6 are not contributing. Both the relaxation times and chemical shift data are thus consistent with the observed total entropy change of 99.5 $\mathrm{JK^{-1}\ mol^{-1}}$ resulting from the two mesophase transitions.

Bromide. The ^{13}C CP-MAS NMR spectrum at 310 K, shown in Figure 6, is quite different from that for the iodide. The chemical shifts at room temperature for all six carbon atoms (Table VIII) are smaller than those for the iodide (Table IX), but are comparable to those of the iodide in the melt, suggesting that the bromide has already achieved a high degree of disorder. Another interesting feature of the room temperature spectrum of the bromide is that C-4 shows at least two peaks (at 33.22 and 31.71 ppm). The low-field peak (33.22 ppm) is close to that of C-4 of the iodide in the condis phase (32.40 ppm at 364 K, Table IX), while the up-field peak (31.71 ppm) is almost the same as that of C-4 of the iodide in the melt (31.87 ppm at 380 K, Table IX). The spectra of Figure 6, reveal that the two peaks of C-4 undergo a coalescence with increasing temperature, and finally merge to 32.07 ppm in the melt (374 K).

Attempting to find the cause for the change in the chemical shift of C-4 in the conformational motion about the bond C2—C3, one must look for some change in the chemical shift for C-1 since C-1 and C-4 are both in γ-position to each other. The change in the chemical shift of C-1 by an amount of about 1 ppm is, indeed, observed within the same temperature range. The chemical shifts for the remaining carbon atoms are practically unchanged. Thus, the transition at 315 K with an entropy of 38 $\mathrm{JK^{-1}\ mol^{-1}}$ can be linked to a good degree of the onset of conformational motion and disorder about the bond C2—C3 which is, as the innermost potentially mobile bond, the last expected to become conformationally disordered. Since the coalescence of the signal for C-4 extends up to 357 K, the transition, centered at 315 K, can only be the beginning of a gradual process and its completion should also be supported by heat capacity studies, presently in progress.

Since the bond C2—C3 becomes disordered at temperatures above 310 K, one expects that the other two disorderable bonds, namely, C3—C4 and C4—C5, become disordered below 310 K. The total entropy of all four transitions that occur below 310 K amounts to, however, only 48.8 JK^{-1} mol^{-1}, which is sufficient only for conformational disordering of about one bond per alkyl chain, rather than two.

To find out at what temperature the bonds C3—C4 and C4—C5 change their conformations, another variable-temperature ^{13}C CP-MAS NMR experiment was conducted by cooling from 310 to 148 K. The spectra are shown in Figure 7. At the lowest temperature, both the appearance of the spectrum and the chemical shifts of all carbon atoms are similar to the iodide at room temperature. Therefore, one can conclude that the bromide is a well-ordered crystalline phase at this temperature. The resonances of the crystalline phase become observable already at 247 K. The spectra obtained between 247 and 310 K are a series of continuous intermediates between the low-temperature crystal and the room-temperature condis phases, suggesting that the transition is largely gradual, interrupted occasionally by the disordering transitions listed in Table VIII. The differences in the spectra between 310 K and 247 K can be interpreted by the combined effect of both conformational motion about the bonds C3—C4 and C4—C5, registered by the chemical shift changes of C-2/C-5 and C-3/C-6, respectively, in addition to some crystal structure changes which influence all carbon atoms. The observed transitions at 148, 167, and 196 K in the DSC experiments are, however, not clearly reflected in Figure 7, because together they have an entropy change only large enough to account for the conformational change of little more than one bond per alkyl chain. Almost as much entropy-increase must thus occur outside of the transition regions and should be observable by heat capacity analysis.

The disordered state at room temperature can be preserved when quenching the sample. A quenching experiment is demonstrated in Figure 8 by a series of ^{13}C CP-MAS NMR spectra obtained on cooling with approximately 60 K/min from 271 to 146 K (bottom four spectra). These four spectra show the effect of fast cooling, i.e., formation of a condis glass. The spectrum at 146 K in Figure 8 shows the same chemical shifts for all carbon atoms as at 228 K. The increased line broadening at low temperatures is typical for materials in the glassy state. By heating the quenched sample from 146 K at a sufficiently slow rate, the glassy material undergoes a so-called "cold crystallization," as is illustrated by the six spectra at the top of Figure 8. The spectrum at 232 K is still a typical amorphous glass, but the spectrum at 244 K has sharper resonances (especially for the outer carbon atoms, presumably because of motional averaging). As the temperature is increased further to 259 K, and eventually to 278 K, the spectra for the ordered crystalline phase can be observed (compared to Figure 7 at 247 K and lower). Such discrepancy in the "crystallization" temperature between heating and cooling is often noted for polymers. As the temperature is further increased to 310 K, the crystalline phase disappears again. The spectrum of 310 K in Figure 8 is the same as that of a fresh sample (Figure 6). The glass transition temperature of the 271 K condis crystal can thus be estimated to occur at about 230 K and the cold crystallization at 260 K.

Tetra-*n*-heptylammonium Bromide and Iodide

Bromide. At room temperature, the bromide shows almost no cross-polarization efficiency, indicative of the presence of a motion in the kHz range that reduces the value of $T_{1\rho H}$ to very short values ($T_{1\rho H}$ is the proton spin-lattice relaxation time in the rotating frame). The spectrum measured with BILEV, shown in Figure 10, indicates broad peaks for all carbon atoms (because of the kHz motion). The chemical shift values listed in the figure are, however, close to the iodide at the same temperature (see Table XI). The thermal transitions are also similar for both bromide and iodide.[1] The conformational motion and disorder is, therefore, expected to be similar for both cases. For these reasons, a detailed analysis will be carried out only for the iodide.

Iodide. In the tetra-*n*-heptylammonium cation, four bonds per alkyl chain are expected to disorder in going from a well ordered crystalline state to the isotropic melt. These bonds are, C2—C3, C3—C4, C4—C5, and C5—C6. In the DSC experiment one observes two transition regions. A first disordering at T_{d1} = 355.4 K with an entropy change of only 26.1 JK^{-1} mol^{-1}, and a second of two overlapping transitions at T_{d2} = 391.0 K and T_i = 398.7 K with entropy changes of 6.2 and 97.9 JK^{-1} mol^{-1}, respectively. After subtracting the entropy for positional disordering (ca. 21 JK^{-1} mol^{-1}) and orientational disordering (20–50 JK^{-1} mol^{-1}) from the combined entropy change of the latter two transitions of 104.1 JK^{-1} mol^{-1}, one obtains entropy changes for conformational disordering only of 33.1–63.1 JK^{-1} mol^{-1}, which is sufficient for only about one bond per alkyl chain becoming disordered in these transitions. This bond is C2—C3, as can be seen from the T_1 values for C-2 and C-3 in going over 395 K to 405 K (see Table XII). At 395 K, C-2 and C-3 have similar T_1 values, while at 405 K (above the isotropization), the difference is obvious.

The three outer bonds, C3—C4, C4—C5, and C5—C6, must thus have been disordered at temperatures lower than T_{d2} (391.0 K). There is, indeed, the low-temperature transition at T_{d1} of 355.4 K, it shows, however, a rather small entropy change, 26.2 JK^{-1} mol^{-1}, and is insufficient to account for even one full bond per alkyl chain becoming disordered. The situation of "entropy deficit" was encountered above in $(C_5H_{11})_4NBr$ and $(C_6H_{13})_4NBr$, and similarly in another small, liquid crystal forming molecule, N,N'-bis(4-*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD), that shows additional condis crystal polymorphs at low temperature.[20] A macromolecule with phenylene, ether, and methylene sequences, MBPE-9, forming condis crystals below the melting transition could also be proven to have such entropy deficit.[21] In all examples it could be shown by variable-temperature solid-state ^{13}C NMR and comparison between the experimental and calculated heat capacities that the disordering between some single C—C bonds occurs gradually, i.e., over a wide range of temperatures without transition. For the tetra-*n*-heptylammonium cation under consideration, the same analyses is attempted next.

The variable-temperature NMR spectra measured from 180 to 310 K (considerably below T_{d1}), shown in Figure 11, show little changes in chemical shift. The numerical values of chemical shift of each carbon atoms are listed in Table XI. Only C-6 and C-7 show noticeable changes. At 180 K, C-6 resonates at 26.22 ppm and is separated from C-2 (at 25.21 ppm). As temperature increases to 290 K, the signal of C-6 becomes gradually superimposed on C-2 (at 25.74 ppm). The two signals of C-7 (the methyl carbon) experience also a gradual up-field shifting. Difference for both C-6 and C-7 between 290 and 180 K are too small (<0.5 ppm) to account for conformational disordering, thus below T_{d1} the iodide forms an ordered phase in which motion is allowed only in the end groups.

The first phase transition on heating (355.4 K) is reflected by changes in the variable temperature ^{13}C NMR spectra from 322 to 364 K (Figure 12). The changes in chemical shift from 322 to 364 K for the carbon atoms are: C-1, -2.67 ppm; C-2, -0.17 ppm; C-3, $+0.01$ ppm; C-4, -1.05 ppm; C-5, -0.72 ppm; C-6, -0.97 ppm; and C-7, -0.27 ppm. These changes can not be interpreted exclusively by the γ-gauche effect, therefore, the cause for this low-temperature transition must be a combined effect of conformational and packing changes. In fact, one finds the following: the largest change for C-1, small changes for C-2, C-3 and C-7, and moderate changes for C-4, C-5 and C-6. The chemical shift of C-1 is largely influenced by its partial positive charge, not by the change in the rotational state of the bond C2—C3, since this bond is known not to be flexible below the high-temperature transition. Thus, a re-distribution of the charge on C-1 is plausible. The charge redistribution on C-1 arises if the anion, I^-, changes its position in the crystal relative to the C-1. The approximately 1 ppm changes in chemical shifts in the outer carbon atoms, C-4, C-5, and C-6, are not likely to be due to the anion positional change, since they are practically neutral carbons. Because C-2 and C-3 are less charged atoms and, at the same time, are also remote from the mobile chain end, their chemical shifts are influenced less by the inter-ion distance change and little by the conformational motion. The same is true even when considering the wider range of temperatures from 180 to 385 K. The methyl carbon, C-7, shows a pattern changes from a doublet at and below 310 K to a single line at 364 K and higher, and the average chemical shift decreases by 1.67 ppm between 180 and 385 K, indicative of its large mobility due to rotations about its C_3-axis as well as motion above C5—C6. Results of X-ray structure analysis are needed for a more detailed explanation for the changes of chemical shift that could not be interpreted by the conformation-dependent γ-gauche effect.

Of particular interest is the behavior of the high-temperature condis phase formed between $T_{d1} = 355.4$ K and $T_{d2} = 391.0$ K. Except for C-1, the chemical shifts of all other carbon atoms in the heptyl chain undergo further up-field drifting as temperature is increased from 364 to 385 K (Figure 12 and Table XI). The chemical shift changes are comparable to or larger than that observed at T_{d1} (355.4 K). These sizeable gradual changes are indicative of a development of conformational disordering. This conclusion is supported by the mobility seen from the ^{13}C NMR powder spectra measured on a static sample shown in Figure 13. The conformational motion in the heptyl chain at 366 K averages the chemical-shift anisotropy interactions to such a degree that the spectral lines are much more resolved than at 310 K. Since the chemical shift anisotropy of a rigid methylene carbon is expected to extend over ca. 40 ppm (2 kHz at 4.7 Tesla),[22] the time scale of the motion of the carbon atoms that show well resolved signals of 366 K must be about 1/(2 kHz) or 500 μs. Condis crystals with motion of such an intermediate mobility show both CP and BILEV signals, as is demonstrated in the spectra of Figure 13 (see also the spectra for $(C_4H_9)_4NBr$ in Figure 1 at 384 K).

Finally, the large chemical shift changes are found at the overlapping transitions ranging from T_{d2} (391.0 K) to T_i (398.7 K). The loss of positional, orientational, and the remaining conformational order between the bonds C2—C3 must be responsible for the observed changes in entropy and the chemical shifts shown in Table XII.

In summary, tetra-*n*-heptylammonium iodide is a condis crystal below its isotropization, and never a plastic crystal. The conformational motion and disorder is developed to a large extent gradually between the two disordering transitions. This observation explains the entropy deficit observed at the phase transition by DSC. Further support for this surprising discovery will be shown by X-ray diffraction[16] and heat capacity analyses,[23] presently in progress. Based on the similar entropy data and ^{13}C chemical shift values measured at room-temperature, the tetra-*n*-heptylammonium bromide is expected to also have a gradual conformational disordering process occurring either below the low-temperature transition (339.5 K) or between the disordering transition and isotropization (366.5 K).

CONCLUSIONS

In the intermediate chain length tetra-*n*-alkylammonium bromides and iodides, two types of mesophases are possible below the isotropization temperature: plastic crystals with orientational and conformational disorder and motion, and condis crystals with conformational disorder only. Furthermore, the condis crystals may be quenched to glasses.

In tetra-*n*-butylammonium iodide, the molecules become orientationally and conformationally disordered in a single crystal-to-plastic-crystal transition. The plastic crystal in $(C_4H_9)_4NI$ has a maximum degree of conformational disorder (one bond per butyl chain). In tetra-*n*-butylammonium bromide, although the mesophase is a condis crystal, it shows considerable orientational motion (libration) introduced gradually as a function of temperature.

As the alkyl chain-length becomes longer, complete orientation and positional disordering takes place only on isotropization. Below T_i, the molecules may still be disordered conformationally (condis crystal). The conformational disordering occurs differently for different crystals.

In the tetra-*n*-pentylammonium salts, one of the two disorderable bonds per alkyl chain gains conformational disorder on isotropization at T_i, while the other one becomes gradually disordered for the bromide (without transition), and for the iodide disordered in one step during a low-temperature transition with the expected entropy.

In tetra-*n*-hexylammonium iodide, all three disorderable bonds of the hexyl chain become conformationally disordered below T_i through two overlapping transitions. In tetra-*n*-hexylammonium bromide the conformational disordering is more complicated. Two of the three disorderable bonds of the hexyl chain become disordered more or less gradually at lower temperatures, and the other one is also disordered largely gradually, however, at higher temperatures. The condis phase of the bromide can be quenched to a glass.

In tetra-*n*-heptylammonium iodide, the conformational disordering of the outer bonds occurs to a large extent gradually between the two disordering transitions.

Of the two relatively small disordering transitions T_{d1} and T_{d2}, the first is likely to be caused mainly by anion rearrangement, and initiates the conformational disordering of the outer bonds. The other (together with isotropization) causes the disordering of the innermost potentially mobile bond C2—C3. The bromide is expected to behave similarly.

In the cases of gradually gaining conformational disorder, e.g., in tetra-*n*-pentylammonium bromide, tetra-*n*-hexylammonium bromide, and tetra-*n*-heptylammonium iodide, heat capacity studies are in progress in this laboratory to support the NMR conclusions with quantitative entropy information.

Acknowledgment

This work was supported by the Division of Materials Research, National Science Foundation, Polymers Program, Grant #DMR 8818412 and the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Professor G. Janz (Rensselaer Polytechnic Institute) is acknowledged for providing some of the samples.

References

1. A. Xenopoulos, J. Cheng, M. Yasuniwa and B. Wunderlich, *Mol. Cryst. Liq. Cryst.*, (Paper I) in press.
2. J. Cheng, A. Xenopoulos, and B. Wunderlich, *Mol. Cryst. Liq. Cryst.*, (Paper II) in press.
3. A. L. van Geat, *Abstracts of the 10th Experimental NMR Conferences,* Mellon Institute, Pittsburgh, PA, March, 1969.
4. F. Coletta, G. Moro and P. L. Nordio, *Mol. Phys.*, **61**, 1259 (1987).
5. J. W. Richards, *Chem. News,* **75**, 278 (1897).
6. P. Walden, *Z. Elektrochem,* **14**, 713 (1908).
7. B. Wunderlich and J. Grebowicz, in *Liquid Crystalline Polymers II/III,* M. Gordon and N. A. Plate, eds., p. 1, *Advances in Polymer Sci.*, **60/61**, Springer Verlag, Berlin, Heidelberg, 1984.
8. B. Wunderlich, *Macromolecular Physics,* Vol. 3 "Crystal melting," Academic Press, New York, N.Y., 1980.
9. B. Wunderlich, M. Möller, J. Grebowicz and H. Baur, *Conformational Motion and Disorder in Low and High Molecular Mass Crystals,* Springer Verlag, Berlin, 1988 (*Adv. Polymer Sci.,* Vol. 87).
10. J. Cheng, A. Xenopoulos and B. Wunderlich, *Magn. Res. in Chem.*, to be published, 1992.
11. D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
12. A. E. Tonelli, "NMR Spectroscopy and Polymer Microstructure: The Conformational Connection," VCH Publishers, New York, 1989.
13. F. A. Bovey, *Chain Structure and Conformation of Macromolecules,* Academic Press, New York, 1982.
14. P. J. Flory, "Statistical Mechanics of Chain Molecules," Wiley-Interscience, New York, 1969.
15. E. Wait and H. M. Powell, *J. Chem. Soc.*, 1872 (1958).
16. A. Habenschuss, A. Xenopoulos and B. Wunderlich, "X-ray diffraction," work in progress.
17. M. Yasuniwa, "X-ray single crystal structure determination work," in progress.
18. J. R. Lyerla, Jr. and G. C. Levy in "Topics of Carbon-13 NMR Spectroscopy," Vol. 1, (G. C. Levy, ed.), John Wiley & Sons, New York, 1974.
19. N. Boden, "NMR Studies of Plastic Crystal," in *The Plastically Crystalline State* (*Orientationally-Disordered Crystals*), (J. N. Sherwood ed.), John Wiley and Sons, Chichester, (1979).
20. J. Cheng, Y. Jin, G. Liang and B. Wunderlich, *Mol. Cryst. Liq. Cryst.*, in press.
21. J. Cheng, Y. Jin, B. Wunderlich, S. Z. D. Cheng, M. A. Yandrasits, A. Zhang and V. Percec, *Macromolecules,* to be published, 1992.
22. L. W. Jelinski and M. T. Melchior, in *NMR Spectroscopy Techniques* (C. Dybowski and R. L. Lichter, eds.), Marcel Dekker, Inc., New York and Basel, 1987.
23. A. Xenopoulos and B. Wunderlich, "Heat capacities of tetraalkylammonium halides," in progress.