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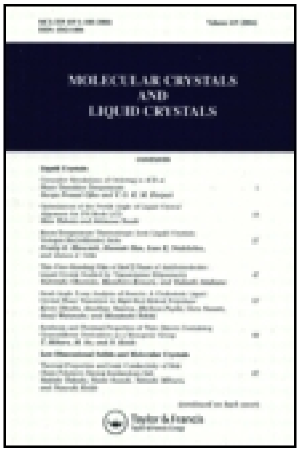

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Condis Crystals of Small Molecules III. Thermal Analysis of Plastic and Condis Crystals of some Cyclosilanes

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Condis Crystals of Small Molecules III. Thermal Analysis of Plastic and Condis Crystals of some Cyclosilanes

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Three cyclic methyl and ethyl substituted silanes were synthesized and their thermal properties analyzed. All show a plastic crystalline state which permits also ring and/or side-chain conformational motion as judged from the enthalpies of transition to the isotropic state. Heat capacity data and entropies of disordering into the plastic crystal leave open the possibility of a condis (conformationally disordered) state below the plastic crystal state with a continuous, transitionless freezing of the conformational motion at lower temperature.

1. INTRODUCTION

In the first paper of this series it was shown that there are three basic mesophases, distinguished from the fully ordered crystal and the fully disordered, amorphous states by either some orientational order

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only (liquid crystals), full positional order, but no orientational order (plastic crystals), or some conformational disorder only (condis crystals).[1] It could be illustrated on the example of N,N′-bis(-4,4′-(*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD) that nematic and smectic liquid crystals always have a large amount of conformational freedom and that at temperatures below the existence range of the most ordered smectic phase, it is still possible to have condis polymorphs.[2] In this and the following paper[3] we would like to present a study of the thermal properties of dodecamethylcyclohexasilane ($M_{12}Si_6$), 1,2,3,4,5,6-hexaethyl-1,2,3,4,5,6-hexamethylcyclohexasilane ($E_6M_6Si_6$) and decaethylcyclopentasilane ($E_{10}Si_5$). These three compounds are easily recognized as plastic crystals, but possess also the possibility of conformational mobility. Thermal analysis, and even more so solid state NMR, discussed in paper IV,[3] make it likely that at least in some of these cyclosilanes conformational motion is introduced at temperatures lower than the transition to the plastic crystal. In addition, it will be shown that this conformational motion begins gradually, over a wide temperature range.[3]

2. EXPERIMENTAL

Decaethylcyclopentasilane ($E_{10}Si_5$)[4] and 1,2,3,4,5,6-hexaethyl-1,2,3,4,5,6-hexamethylcyclohexasilane ($E_6M_6Si_6$)[5] preparations have been reported earlier by West et al. The samples used in this research have been prepared independently for a prior publication,[6] the preparation is described below for the first time:

In a typical reaction, 125 ml tetrahydrofurane was distilled into a flame-dried reaction flask fitted with an additional funnel, glass-blade stirrer, reflux condenser, and immersed thermometer. A dry argon atmosphere was maintained in the reaction vessel. Potassium (6.6 g, 0.17 mole), sodium (1.4 g, 0.06 mole) and 0.2 g naphthalene was added. The mixture was heated to mild reflux with stirring until the NaK-alloy formed and the dark color of alkali metal-naphthalide was present. The heating was then reduced and diethyldichlorosilane added dropwise (15.0 ml, 0.10 mole) so that the mild reflux was maintained (about 45 min.). After complete addition, the reflux was maintained for 4 h by increased heating. The cooled reaction mixture was carefully chilled in an external ice-water bath until the flask temperature approached 0°C. Glacial acetic acid (5 ml) in tetrahydrofurane (10 ml) was added dropwise to terminate the reaction and consume excess alkali metal. The reaction mixture changes then from dark to pale orange. After warming to ambient temperature, the reaction mixture

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was diluted with 100 ml of *n*-hexane and washed sequentially with 200 ml water, 200 ml 10% aqueous $NaHCO_3$, and 200 ml saturated, aqueous, NaCl. The organic layer was dried over 50 g Na_2SO_4, filtered and passed through a column of 200 g of activated, neutral alumina. The column was washed with 300 ml additional *n*-hexane. The organic solution was evaporated to yield a viscous oil (8.0 g, 93%) which was a mixture of diethylsilane rings (IR, gas chromatography-mass spectrometry). Dominating were $E_{10}Si_5$ (90%) and $E_{12}Si_6$ (8%).

The crude reaction mixture was distilled at reduced vacuum (about 0.2 mm Hg) through a 20 cm heated column packed with glass beads and heated still head. Fractions boiling to 190°C were set aside. One main fraction boiling at 190–200°C was collected (4.55 g, 53%). This fraction was shown to be $E_{10}Si_5$ of >99% purity by IR and gas chromatography—mass spectrometry.

Similarly ethylmethyldichlorosilane (13.5 ml, 0.10 mole) yielded 6.8 g (94%) of a viscous oil which was shown to contain $E_5M_5Si_5$ (62%) and $E_6M_6Si_6$ (28%) and other rings. The reaction mixture was distilled at reduced pressure (0.2 mm Hg) using the apparatus described above, to yield in the 160–190°C fraction pentamer and hexamer only (5 g, 70%). A final distillation fraction collected at 190–200°C was shown by gas chromomatography—mass spectrometry to be $E_6M_6Si_6$ in purity >98%. The yield of this fraction was 1.1 g (15%). The sample was also analyzed by IR.

The preparation of $M_{12}Si_6$ followed closely the method reported by Carberry and West.[7]

Thermal analysis was performed with two calorimeters. Transition behavior was studied with a Dupont 990 Thermal Analyzer coupled to a DSC-cell. A computer interfaced Perkin-Elmer DSC-4 was used for heat capacity measurements. Hardware and software for the computer was designed by Laboratory Microsystems. The temperature scales were calibrated with high purity melting standards (lead, tin, indium, benzoic acid, naphthalene, *n*-dodecane, and cyclohexane). All analyses were run in hermetically sealed pans and under nitrogen atmosphere.

The transitions were identified using a Leitz polarizing microscope with a Mettler FP52 hot-stage.

A Varian XL-200 NMR spectrometer was used to measure the ^{13}C spectra using a 70 g/l solution in deuterated toluene in the temperature range 230 to 360 K. The samples were run under the conditions: frequency 50 MHz, acquisition times 4s, sweep width 3000 Hz, phase delay 4s, pulse-width 40° and 5.0 μs.

3. RESULTS

Scanning calorimetry

All measurements were carried out from liquid nitrogen temperature to a high-temperature limit set by beginning weight-loss (deduced from thermogravimetry). Figures 1 to 3 show sample DSC-traces of the three cyclosilanes cooled at different rates. The transition temperatures, heats of transition and entropies, calculated under the assumption of equilibrium, are listed in Table I. Less likely entropy values, because of deviation from equilibrium conditions, are placed in parentheses. Heat capacities of the samples pretreated to be closest to equilibrium are given in Table II.

The two endotherms in each sample separate three phases. The low temperature phase will be called I. It changes at T_d, the disordering temperature, to the intermediate phase II. This changes at T_i, the temperature of isotropisation, to the high temperature phase,

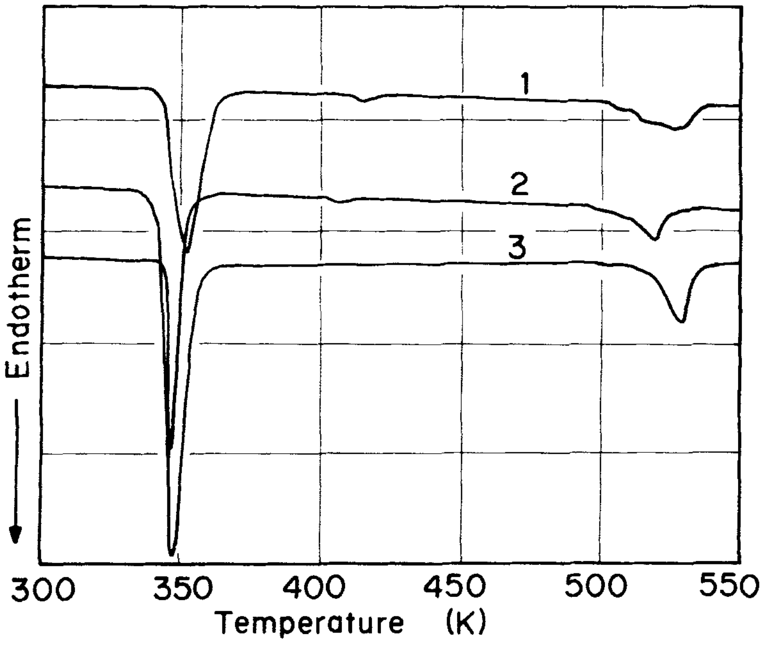

FIGURE 1 DSC-Curves of $M_{12}Si_6$ heated at 20 K/min (duPont DSC). Curve 1: Sample as synthesized, after cooling at about 30 K/min from room temperature to 120 K. Curve 2: After cooling at 20 K/min from 573 to 120 K. Curve 3: After quenching from 573 to liq. N_2 temperature.

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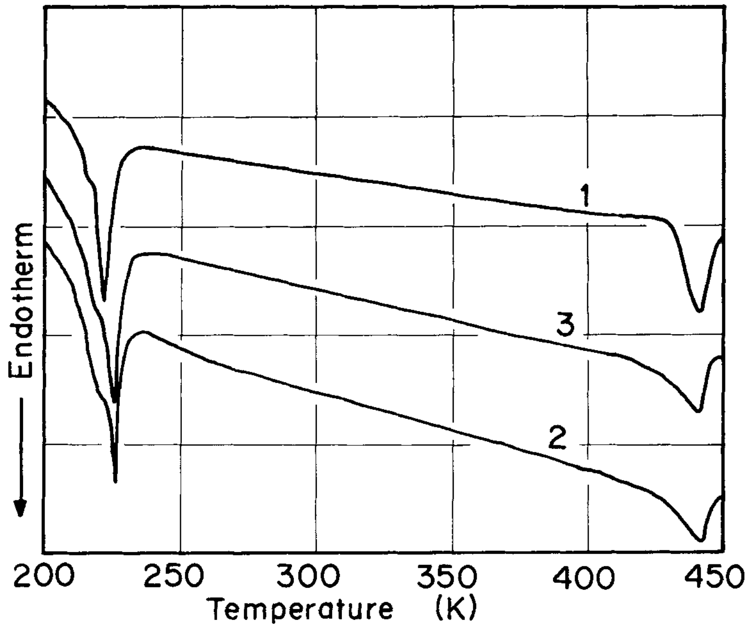

FIGURE 2 DSC-Curves of $E_6M_6Si_6$ heated at 20 K/min (duPont DSC). Samples 1–3 pretreated as $M_{12}Si_6$ in Figure 1. Isotropic melt starting temperature 453 K.

easily identified by inspection and optical microscopy as the isotropic, liquid state. Macroscopically, phase II is extremely easily deformed and has lead to the earlier naming of the phase as a plastic crystal.[8]

$M_{12}Si_6$ showed birefringence in the monoclinic phase I, as expected, but not in the phase II, the mesophase. Similarly, $E_6M_6Si_6$ and $E_{10}Si_5$ showed no birefringence in their phases II. In the latter case phases I are stable only below the temperature range of our microscope, so that no information on the possible birefringence of their crystals could be gained.

Figure 4 shows the solution ^{13}C NMR spectrum of $Me_{12}Si_6$ from 313 to 233 K. Some broadening can be observed below 273 K, but the sensitivity is not enough to say with certainty that rotational isomers do not interconvert in the time scale of the NMR experiment even at 233 K. A similar conclusion based on solution NMR and ESR was reached earlier by West and Glass.[10] If there should be distinct rotational isomers in the crystal above this temperature, they would have to be imposed by intermolecular forces. It will be shown in paper IV of this series using solid state ^{13}C NMR that, indeed, fixed rotational isomers exist only below 280 K.

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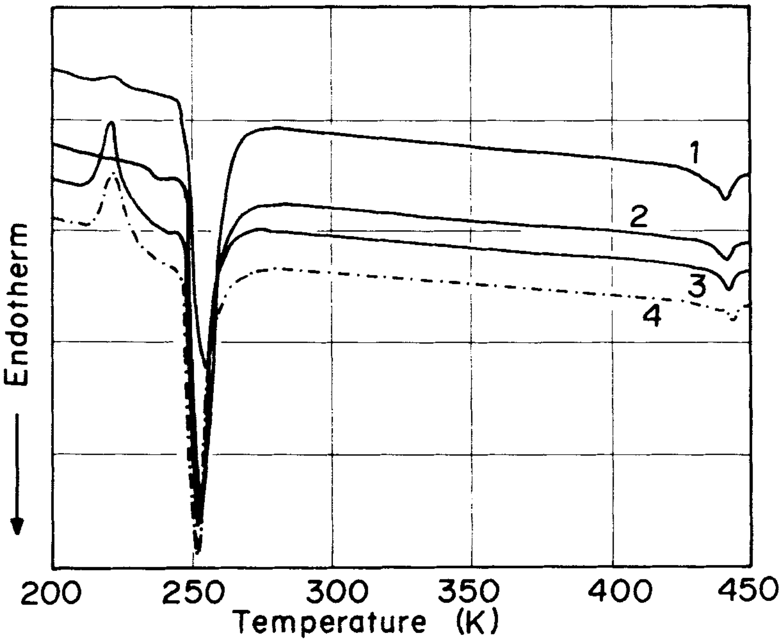

FIGURE 3 DSC-Curves of $E_{10}Si_5$ heated at 20 K/min. Curves 1–3 as in Figures 1 and 2. Curve 4 after quenching from 380 K to liq. N_2 temperature.

4. DISCUSSION

Figures 1 to 3 and the data in Table I make it clear that the high temperature transition from phase II to the melt is much less than 21 J/(K mol), Timmermanns' original criterion for a plastic crystal.[11] More precisely, one can state that the melting of spherical atoms or molecules is to have an entropy of fusion of 7–14 J/(K mol)[12] (Richards' Rule). While $M_{12}Si_6$ may still be within this limit, $E_6M_6Si_6$ and $E_{10}Si_5$ are much below it. We must draw two conclusions from these data: first, that any conformational motion possible in the melt is also possible in the crystal phase II since the low entropy of transition does not permit additional disordering; second, that even the positional disordering is less than needed for complete disordering, which means that considerable positional disorder must exist in crystal phase II. The second conclusion is seen macroscopically by exceedingly high plasticity, making the crystals even flow in the bottle. The ease of conformational changes in the Si_6-ring can be judged from the solution NMR-data of Figure 4, and the orientational disorder in $M_{12}Si_6$ was proven by proton NMR earlier.[13] The plastic crystalline

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TABLE I

Summary of thermal analysis data

Sample	Thermal history	T_d (K)	ΔH_d (kJ mol^{-1})	ΔS_d (J mol^{-1}K^{-1})	T_i (K)	ΔH_i (kJ mol^{-1})	ΔS_i (J mol^{-1}K^{-1})
$M_{12}Si_6$[a]	As made	352.4	16.7	47.4	528.8	4.2	7.9
	Cooled 20 K/min	346.4	16.7	(48.2)	520.1	3.0	(5.8)
	Quenched	347.1	16.8	(48.4)	528.0	3.8	(7.2)
$E_6M_6Si_6$[b]	Cooled from RT 30 K/min	222.1	3.6	(16.2)	439.2	1.8	4.1
	Cooled 20 K/min	226.3	3.8	16.8	437.2	1.5	(3.4)
	Quenched	226.3	4.5	(19.9)	437.2	1.5	(3.4)
$E_{10}Si_5$[c]	Cooled from RT 30 K/min	255.2	16.3	(63.9)	440.1	1.4	3.2
	Cooled 20 K/min	254.8	16.3	64.0	440.1	0.9	(2.0)
	Quenched isotropic	252.4	13.0	(51.5)	442.5	0.8	(1.8)
	Quenched mesophase	251.9	11.6	(46.1)	442.8	0.8	(1.8)

[a] Compare to curves 1 to 3 of Figure 1.

[b] Compare to curves 1 to 3 of Figure 2.

[c] Compare to curves 1 to 4 of Figure 3. The exotherm(s) are as follows: curve 1, 221 K, 0.2 kJ/mol; curve 3, 174 and 221 K, 1.9 and 2.8 kJ/mol, respectively; curve 4, 174 and 222 K, 2.5 and 3.2 kJ/mol, respectively.

TABLE II

Heat capacities of $M_{12}Si_6$, $E_6M_6Si_6$, and $E_{10}Si_5$ [a]

Temperature (K)	$M_{12}Si_6$ ($J\ K^{-1}mol^{-1}$)	$E_6M_6Si_6$ ($J\ K^{-1}mol^{-1}$)	$E_{10}Si_5$ ($J\ K^{-1}mol^{-1}$)
140	359	494	415
150	362	532	439
160	365	575	460
170	368	626	480
180	372	682	498
190	377	745	514
200	382	815	528
210	387	(987)	541
220	393	(820)	(483)
230	399	(800)	572
240	405	813	(602)
250	420	828	(1683)
260	433	844	(1301)
270	448	855	765
280	459	860	774
290	483	867	786
300	503	872	796
310	527	870	805
320	553	871	812
330	571	872	821
340	(686)	871	831
350	(3416)	867	841
360	(652)	858	849
370	659	843	865
380	671	837	873
390	686	848	884
400	701	862	898
410	696	878	913
420	700	(895)	932
430	713	(933)	(968)
440	720	—	—
450	726	—	—
460	735	—	—
470	746	—	—
480	751	—	—
490	766	—	—
500	(793)	—	—

[a] Values in parentheses are single or only partially averaged heat capacity amplitudes in the transition area and at the start of measurement, respectively. All other values are averaged over the ±5 K range from the computer output.

state in the cyclosilanes permits thus also conformational interchange. A more detailed proof is given in paper IV of this series on the basis of solid state NMR.[3]

The next question to be asked concerns the motion introduced at the disordering transition. Both $M_{12}Si_6$ and $E_{10}Si_5$ show an entropy

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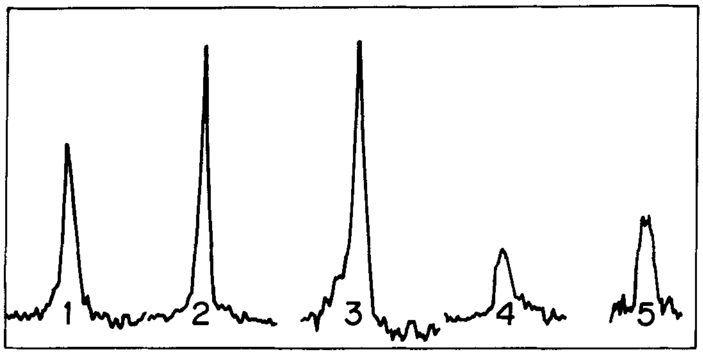

FIGURE 4 ^{13}C NMR spectra of $M_{12}Si_6$ in D-toluene at 313 K (curve 1), 293 K (2), 273 K (3), 253 K (4), and 233 K (5).

of transition (ΔS_d, Table I) sufficient to account for a rigid, nonspherical molecule to obtain orientational freedom as expected for a plastic crystal. A survey of 26 such molecules showed total entropies of fusion between 21 and 59 J/(K mol).[12] Subtracting the positional contribution of 7–14 J/(K mol) leads to the magnitude of entropy change found for ΔS_d (see Table I). But both, $M_{12}Si_6$ and $E_{10}Si_5$, may contain in addition to the orientational contribution some contribution from conformational changes. As many as 24 boat, chair and twist conformations in $M_{12}Si_6$, and 3^5 rotational -C_2H_5 conformations in the $E_{10}Si_5$ molecule. In both cases ΔS_d is on the low side to account for additional, full excitation of the conformational changes which would be 24 and 46 J/(K mol). Only additional direct evidence on motion can resolve this question, such as solid state NMR, to be described in paper IV.[3] Although X-ray structure determination suggests in crystal form I of $M_{12}Si_6$ a fixed chair conformation, there are some problems remaining in the X-ray analysis which need be resolved.[9] The much lower ΔS_d of $E_6M_6Si_6$ is probably due to disorder in crystal form I which is expected from the packing of the isomerically impure compound. The low T_d is an indication of such poorer crystals.

The heat capacities of the three cyclosilanes in Table II indicate for phases II a shallower slope than for phases I. Such behavior is typical for a more mobile state.

The analyzed low temperature range of phase I of $M_{12}Si_6$ was large enough to check between 140 and 240 K for any possible pretransition gain in entropy. For this purpose the smoothed heat capacity which can be represented within ±0.8% by the equation

$$C_p = 365.9 - 0.351\,T + 2.150 \cdot 10^{-3}T^2\ (\mathrm{J\,K^{-1}mol^{-1}}) \qquad (1)$$

was changed to C_v using the Nernst-Lindemann equation with a universal constant.[14] Next, the heat capacity contributions of the 12 methyl groups involving hydrogens (126 normal modes) were subtracted using the technique developed for the methyl group of polypropylene.[15] The remaining skeletal heat capacity should be caused mainly by 36 vibrations involving Si-Si and Si-C bending and stretching as well as low frequency intermolecular vibrations. This skeletal heat capacity decreases slightly (almost linearly) from 140 K [261 J/(K mol)] to 240 K [211 J/(K mol)]. Although these changes are close to the error limit for measurement and approximate calculation, they do indicate that: a) there is no endothermic entropic pre-transition contribution to the heat capacity in this temperature range; and b) it is likely that the decrease in skeletal heat capacity may signal the change of the Si-C torsional oscillators into hindered rotators with the accompanying decrease in heat capacity from R to R/2.

5. CONCLUSIONS

1. Three cyclic silanes have been synthesized which show a plastic crystalline state.
2. In the plastic crystalline state all three seem to show full conformational freedom. $M_{12}Si_6$ exhibits conformational mobility within the ring; $E_6M_6Si_6$ has both, ring and side-group conformational freedom; $E_{10}Si_5$ only side-group conformational freedom.
3. $E_6M_6Si_6$ and $E_{10}Si_5$ show a reduced entropy of disordering on going to the isotropic state, indicative of an imperfect crystal structure in the plastic crystal state.
4. Heat capacities and entropies of transition leave open the possibility of conformational motion below the plastic crystal phase, i.e. crystal phases I may be condis crystals which lose their mobility without first order transition.

Acknowledgments

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References

1. B. Wunderlich, M. Moeller and H. G. Wiedemann, *Mol. Cryst. Liq. Cryst.*, prior publication.
2. H. G. Wiedemann, J. Grebowicz and B. Wunderlich, *Mol. Cryst. Liq. Cryst.*, prior publication.

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3. M. Moeller and B. Wunderlich, to be published.
4. C. W. Carlson, K. Matsumura and R. West, *J. Orgmet. Chem.*, **194**, C5 (1980).
5. A. Katti, C. W. Carlson and R. West, *H. Orgmet. Chem.*, **271**, 353 (1984).
6. J. P. Wesson and T. C. Williams, *J. Polymer Sci., Polymer Chem. Ed.*, **19**, 65 (1981).
7. E. Carberry and R. West, *J. Am. Chem. Soc.*, **91**, 5440 (1969).
8. D. W. Larsen, B. A. Soltz, F. E. Stary and R. West, *Chem. Commun.*, 1093 (1978).
9. H. I. Carell and J. Donohue, *Acta Cryst.*, **B26**, 1566 (1972).
10. E. Carberry, R. West and G. E. Glass, *J. Am. Chem. Soc.*, **91**, 5446 (1969).
11. P. J. Timmermanns, *J. Phys. Chem. Solids*, **18**, 1 (1961).
12. B. Wunderlich, "*Macromolecular Physics, Vol. 3, Crystal Melting*," Academic Press, New York, 1980.
13. D. W. Larsen, B. A. Soltz, F. E. Starry and R. West, *J. Phys. Chem.*, **84**, 1340 (1980).
14. J. Grebowicz and B. Wunderlich, *J. Thermal Anal.*, **30**, 227 (1985).
15. J. Grebowicz, S.-F. Lau and B. Wunderlich, *J. Polymer Sci.*, Polymer Symposium, **71**, 19 (1984).

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