is to be expected that E' and tan δ, for example, will depend somewhat on time, as well as temperature and frequency, when they are determined on a polymer whose temperature has been changed rather quickly within the glassy state. The extent of the time dependence will depend on many factors, including the time to reach the desired test temperature, the time thereafter before measurements are begun, and the needed time to obtain the data. If measurements are taken during the continuous heating from a low temperature as is often done, the data will be perturbed somewhat by the effects discussed here.

References and Notes

(1) Kovacs, A. J. *J. Polym. Sci., Part C* **1958**, *30*, 131.
(2) Kovacs, A. J. *Adv. Polym. Sci.* **1963**, *3*, 394.
(3) Kovacs, A. J.; Stratton, R. A.; Ferry, J. D. *J. Phys. Chem.* **1963**, *67*, 152.
(4) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, 1978.
(5) Struik, L. C. E. *Polym. Eng. Sci.* **1977**, *17*, 165.
(6) Smith, T. L.; Levita, G.; Moonan, W. K. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 875.
(7) Kovacs, A. J. In Structure and Mobility in Molecular and Atomic Glasses. O'Reilly, J. M.; Goldstein, M., Eds.; *Ann. N.Y. Acad. Sci.* **1981**, *371*, 38–64.
(8) Struik, L. C. E. *Polymer* **1988**, *29*, 1347.
(9) Haidar, B.; Smith, T. L. *Polymer*, in press.
(10) Illers, K. H.; Breuer, H. *Kolloid-Z.* **1961**, *176*, 110.
(11) Ricco, T.; Smith, T. L. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 513.
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Low-Temperature Crystal–Crystal Phase Transitions in Triblock Semifluorinated *n*-Alkanes

Temperature-induced phase transitions have been observed and characterized in *n*-alkanes,[1] perfluoro-*n*-alkanes,[2] and a number of long-chain polymers.[3-5] In a limited number of cases, phase transitions have also been observed when these materials are subjected to high pressure.[6,7] In general, phase transitions may be classified into at least two groups: order–disorder and crystal–crystal transitions. In the former, the lattice structure is preserved, but the conformational order of the chain is altered at the phase transition. On the other hand, at crystal–crystal transitions lattice structural changes occur, but conformational order is preserved although it may change from one ordered form to another. In many cases a crystal–crystal transition gives rise to a different symmetry of the unit cell, which, in turn, manifests itself as a change in the spectroscopic selection rules.

Recently, a series of semifluorinated diblock,[8-11] $F(CF_2)_n(CH_2)_mH$ [FnHm], and triblock,[12] $F(CF_2)_n(CH_2)_m(CF_2)_nF$ [FnHmFn], copolymers have been synthesized and characterized in the solid state and in the melt. In the FnHm diblocks,[9] a high-temperature crystal–crystal phase transition was observed, which was very similar to the "rotator" phase found for many *n*-alkanes. No such transition was observed for their triblock Fn-HmFn analogues. The purpose of this paper is, however, to report the first observation of a low-temperature phase transition in a triblock compound during which a rearrangement of the chains within the unit cell occurs.

The triblock semifluorinated *n*-alkane, F12H10F12, used in this study was synthesized from perfluorododecyl iodide and 1,9-decadiene in a procedure analogous to that utilized for the preparation of other F12HmF12 compounds.[12] A detailed description of the instrumentation used for the variable-temperature measurements contained in this work has been given previously.[8]

As shown in Figure 1, the room-temperature Raman spectra of F12H10F12 can be understood as a simple composite spectrum originating from a superposition of a fluorocarbon and a hydrocarbon spectrum. The sharp bands between 1000 and 1500 cm^{-1} shown in Figure 1 are characteristic of vibrational motions of the $-CH_2-$ hydrocarbon segment with the exception of the narrow symmetric $-CF_2-$ stretching band at 1380 cm^{-1} and the broad feature at 1215 cm^{-1} attributable to CC stretching and CCC bending.[13,14] As can be seen in Figure 1, the spectra at 60 and 14 °C are identical since no high-temperature phase transition, like that which occurs in certain of the diblock FnHm molecules,[9] exists in the triblock F12H10F12. However, in this case a substantial change in the Raman spectrum is observed instead at subambient temperatures. A phase transition occurs below 14 °C (a weak DSC transition is observed at 14–18 °C upon cooling at 10 °C/min) and is manifested by a change in relative intensity of the CC stretching bands in the 1050–1150-cm^{-1} region and the appearance of a sharp band in the $-CH_2-$ bending region at 1415 cm^{-1}. The latter feature

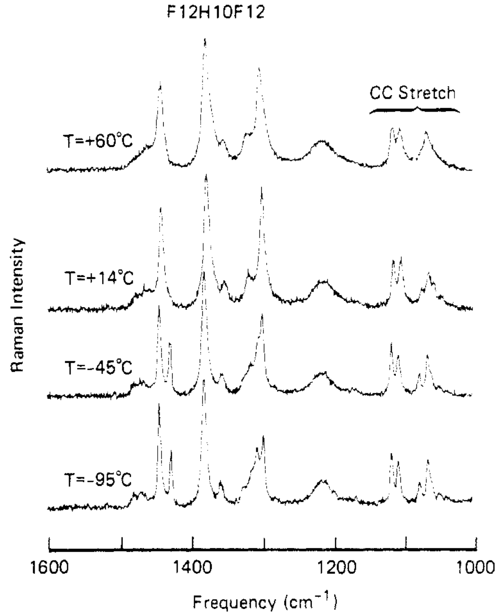

Figure 1. Raman spectra of F12H10F12 obtained as a function of temperature. Data were obtained at 2-cm^{-1} resolution using 200 mW of laser power at 488.0 nm.

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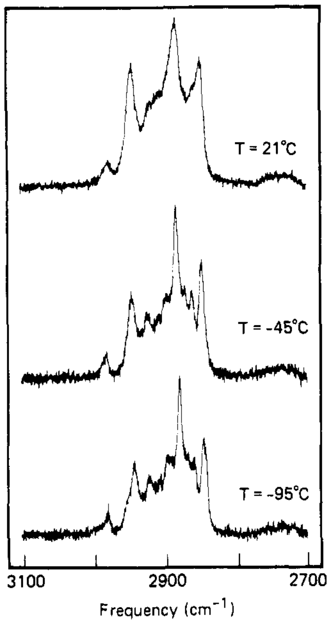

Figure 2. Raman spectra of the CH stretching region of F12H10F12 as a function of temperature.

is known[15] to reflect the lateral packing of $-CH_2-$ groups in an orthorhombic subcell of the crystal lattice arising from a factor group splitting of a $-CH_2-$ bending mode (1440 and 1415 cm^{-1}). This only occurs when the subcell symmetry is orthorhombic and contains at least two molecules.[16]

This behavior is reminiscent of that found for the odd *n*-alkanes, which exist in an orthorhombic phase at room temperature[17] (as indicated by the presence of the 1415-cm^{-1} band) but undergo a transition to a hexagonal phase within a few degrees of their melting point. It appears that the F12H10F12 exists in the hexagonal phase between room temperature and its melting point and has a second, perhaps orthorhombic, phase below room temperature.

This premise is further supported by examination of the $-CH_2-$ stretching region in the Raman spectrum of the triblock shown in Figure 2. At room temperature, the asymmetric $-CH_2-$ stretching vibration near 2880 cm^{-1} is somewhat broad (bandwidth = 15 cm^{-1}; peak position = 2884 cm^{-1}) and only slightly higher in intensity than the symmetric stretch at 2850 cm^{-1}. An identical intensity pattern has been observed[18] for the hexagonal *n*-alkanes and attributed to the absence of intermolecular coupling and the presence of molecular mobility due to the loose packing of chains in the unit cell. As shown in Figure 2, this pattern in the F12H10F12 compound changes dramatically at low temperatures. Upon lowering the temperature to −95 °C, the 2880-cm^{-1} band becomes quite sharp (bandwidth = 7 cm^{-1}; peak position = 2882 cm^{-1}) and assumes the band shape and intensity pattern generally analogous to that found in the room-temperature orthorhombic phase of the odd *n*-alkanes. Recent studies by Zerbi et al.[19] reported similar results for *n*-alkanes that undergo an orthorhombic to hexagonal phase transition. They attributed the changes in bandwidth and peak position of the asymmetric $-CH_2-$ stretching mode observed at the phase boundary to librotorsional motions of the *n*-alkane chains. The longitudinal motion generated in these chains is believed to bring about the formation of the new phase via a surface disordering mechanism.[20] It should be noted that, in the case of F12H10F12, the bands above 2900 cm^{-1} arise from overtones and/or combinations of methylene bending vibrations since no methyl groups are present in the triblock compounds.

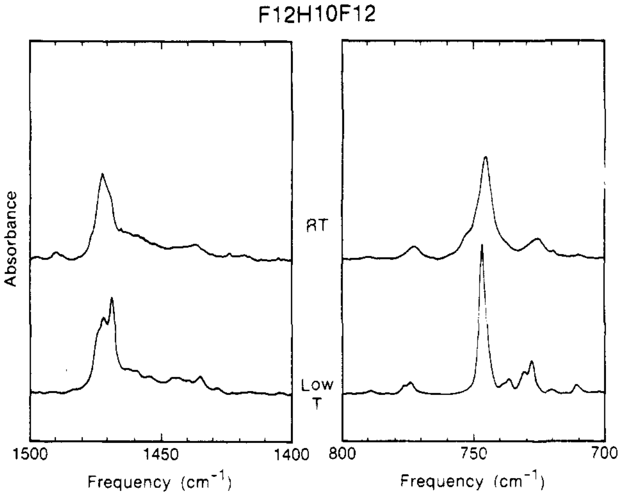

Figure 3. Infrared spectra of F12H10F12 obtained at ambient and low temperature. Spectra were obtained in KBr pellets by using a resolution of 2 cm^{-1} with the coaddition of 256 scans.

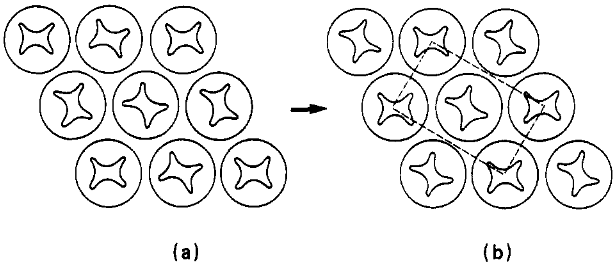

Figure 4. Schematic of the mechanism of the observed phase transition. Cross section of fluorocarbon helix and planar zigzag hydrocarbon: (a) room-temperature phase (chains highly mobile); (b) low-temperature phase (increase in intermolecular forces reduces chain motion and "locks" them into registration, in this case an orthorhombic unit cell).

Additional insight into the origin of this low-temperature phase transition is obtained from the infrared absorbance spectra shown in Figure 3. In this case the $-CH_2-$ rocking region (720–730 cm^{-1}) and the $-CH_2-$ bending region (1460–1470 cm^{-1}) of the F12H10F12 are shown at both ambient and low temperature. In the latter case the temperature was estimated to be lower than −50 °C, well below the observed phase-transition temperature. As can be seen both the $-CH_2-$ rocking and bending vibrations are broad at room temperature, with the bending vibration containing, perhaps, a second component. Upon lowering the temperature these bands are both observed to split into at least two components, giving further evidence for a change in the subcell symmetry. The splittings observed in the low-temperature IR spectrum shown in Figure 3 are analogous to that observed for the room-temperature orthorhombic phase of odd *n*-alkanes[18] and, therefore, suggest that a change in subcell symmetry has occurred in the F12H10F12 below its phase transition.

One possible mechanism for such a crystal–crystal transition in the F12H10F12 is schematically illustrated in Figure 4. In this case the circles represent the cross section of the fluorocarbon helix while the interior structure of the circle represents the planar zigzag conformation of the hydrocarbon chain. At room temperature (Figure 4a) there is considerable mobility of the hydrocarbon chains and they pack into a unit cell, with that angle between their backbone planes being random as shown. At low temperatures, this rotational mobility is considerably reduced due to intermolecular interactions and the symmetry of the unit cell becomes orthorhombic as shown in Figure 4b. This would then explain the change in bandwidth and intensity of the $-CH_2-$ stretching bands, the appearance of the 1415-cm^{-1} band in the $-CH_2-$ bending region of the Raman spectrum, and the splitting observed in the IR spectra at low temperature. A phase transition having many structural similarities has been recently observed in the *n*-alkane clathrates[21] where at low temperature a contraction of the urea lattice increases the intermolecular interaction between *n*-alkane chains, thus also changing the subcell structure.

The exact mechanism of the transition is unclear, but an analogy to that observed by Zerbi et al.[20] for *n*-alkanes may not be drawn due to the thermodynamic incompatibility of hydrocarbon and fluorocarbon chains. Any surface disordering mechanism in the F12H10F12 triblock crystals would involve the longitudinal motion of fluorocarbon segments through a hydrocarbon lattice, which is highly unlikely due to the incompatible nature of these chemical species.

Thus, it has been shown that the F12H10F12 triblock molecule exists in a hexagonal-like structure at room temperature similar to that found for odd *n*-alkanes a few degrees below their melting point. At low temperatures, the F12H10F12 undergoes a transition to a new phase characterized by a decrease in molecular mobility due to an increase in the intermolecular coupling. Spectral observations indicate that this new phase is similar to the orthorhombic phase that exists in the odd *n*-alkanes at room temperature. No specific information was obtained from the Raman spectra of the fluorocarbon portion of the molecule to suggest that it has undergone a conformational change at low temperature, although here some subtle change to allow closer proximity of the hydrocarbon segments may not be spectroscopically detectable. Future studies will address this aspect in more detail.

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References and Notes

(1) Broadhurst, M. G. *J. Res. Natl. Bur. Stand.* **1962**, *66A*, 241.
(2) Vanni, H.; Rabolt, J. F. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 587.
(3) Martin, G. M.; Eby, R. K. *J. Res. Natl. Bur. Stand.* **1968**, *72A*, 467.
(4) Miller, R. D.; Hofer, D.; Rabolt, J. F.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2172.
(5) Tatsumi, T.; Fukushima, T.; Imada, K.; Takayanagi, M. *J. Macromol. Sci., Phys.* **1967**, *B1*, 459.
(6) Bridgman, P. W. *Proc. Am. Acad. Arts Sci.* **1948**, *76*, 71.
(7) Rabolt, J. F.; Piermarini, G.; Block, S. *J. Chem. Phys.* **1978**, *69*, 2872.
(8) Rabolt, J. F.; Russell, T. P.; Twieg, R. J. *Macromolecules* **1984**, *17*, 2786.
(9) Russell, T. P.; Rabolt, J. F.; Twieg, R. J.; Siemens, R. L.; Farmer, B. L. *Macromolecules* **1986**, *19*, 1135.
(10) Viney, C.; Russell, T. P.; Depero, L. E.; Twieg, R. J. *Mol. Cryst. Liq. Cryst.* **1989**, *168*, 63.
(11) Viney, C.; Twieg, R. J.; Russell, T. P.; Depero, L. E. *Liq. Cryst.* **1989**, *5*, 1783.
(12) Twieg, R. J.; Rabolt, J. F. *Macromolecules* **1988**, *21*, 1806.
(13) Boerio, F. J.; Koenig, J. L. *J. Chem. Phys.* **1970**, *52*, 4826.
(14) Rabolt, J. F.; Fanconi, B. *Macromolecules* **1978**, *11*, 740.
(15) Hendra, P. J.; Jobic, H. P.; Marsden, E. P.; Bloor, D. *Spectrochim. Acta* **1977**, *33A*, 445.
(16) Olf, H.; Fanconi, B. *J. Chem. Phys.* **1973**, *59*, 534.
(17) Barnes, J. D.; Fanconi, B. *J. Chem. Phys.* **1972**, *56*, 5190.
(18) Snyder, R. J.; Hsu, S. L.; Krimm, S. *Spectrochim. Acta* **1978**, *34A*, 395.
(19) Zerbi, G.; Roncone, P.; Longhi, G.; Wunder, S. L. *J. Chem. Phys.* **1988**, *89*, 166.
(20) Zerbi, G.; Magni, R.; Gussoni, M.; Moritz, K. H.; Bigotto, A.; Dirlikov, S. *J. Chem. Phys.* **1981**, *75*, 3175.
(21) Casal, H. L.; Cameron, D. G.; Kelusky, E. C. *J. Chem. Phys.* **1984**, *80*, 1407.

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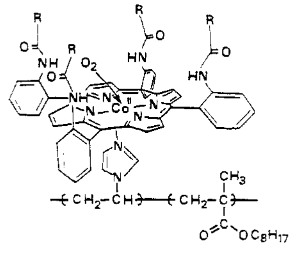
Enhanced Stability and Facilitation in the Oxygen Transport through Cobalt Porphyrin Polymer Membranes

We describe herein the polymer-bound cobalt porphyrin derivatives with large oxygen-binding kinetic constants and with extraordinarily prolonged lifetimes through which oxygen permeates with high selectivity ($P_{O_2}/P_{N_2} > 10$).

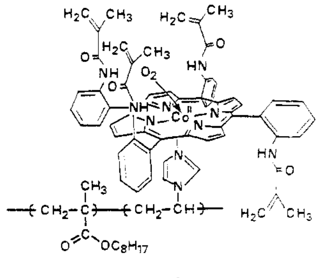
Metalloporphyrin and cobalt–Schiff base chelates with oxygen-binding ability have been applied to an oxygen-transporting fluid[1] and to an oxygen-enriching liquid membrane.[2] But these oxygen-carrying metal chelates in solutions are often irreversibly oxidized and their lifetimes as an oxygen carrier are quite limited. We have recently reported measurements of facilitated oxygen transport in dry (or solvent-free) polymer membranes containing a cobalt porphyrin and a cobalt–Schiff base chelate as a fixed carrier which sorbs oxygen selectively and reversibly.[3] We intended here to enhance the efficiency of this facilitated transport and to prolong the lifetime of the metal chelate as an oxygen carrier. We synthesized the following polymer-bound cobalt porphyrins: *meso*-mono(α-*o*-methacrylamidophenyl)tris(α,α,α-*o*-pivalamidophenyl)-



1a $4R = -C(CH_3)_3$

1b $3R = -C(CH_3)_3$ $1R = -\overset{CH_3}{C}=CH_2$

1c $2R = -C(CH_3)_3$ $2R = -\overset{CH_3}{C}=CH_2$



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