Structural Studies of Semifluorinated *n*-Alkanes. 4. Synthesis and Characterization of $F(CF_2)_nC_6H_4(CF_2)_nF$ by Conventional and Fourier Transform Raman Spectroscopy

A. Schulte, V. M. Hallmark, R. Twieg, K. Song, and J. F. Rabolt*

IBM Research Division, Almaden Research Center, San Jose, California 95120-6099

Received November 1, 1990; Revised Manuscript Received January 29, 1991

ABSTRACT: A series of semiflexible fluorocarbon oligomers containing an aromatic core, $F(CF_2)_nC_6H_4(CF_2)_nF$, have been synthesized and characterized by thermal analysis and both Fourier transform and conventional Raman spectroscopy. Measurements at ambient and low temperature and as a function of pressure were utilized to investigate the impact of the rigid ring on the low-frequency longitudinal acoustic mode (LAM) of the fluorocarbon chain. Normal-coordinate calculations as a function of chain length were performed to provide insight into molecular motion in the low-frequency region.

Introduction

Fluorocarbon oligomers serve as useful model systems to investigate the role of backbone conformation in relation to chain stiffness in semiflexible polymers.[1-3] Previous studies of perfluorocarbon oligomers as well as diblock[4-7] and triblock[8] semifluorinated *n*-alkanes have extensively probed their crystal and conformational structure. Of particular interest in the semifluorinated oligomers was the effect of the semiflexible hydrocarbon block on the frequency and intensity of the Raman active longitudinal acoustic mode (LAM). In these semifluorinated systems, the hydrocarbon block was found to participate in the accordion-like motion characteristic of LAM in the room-temperature solid phase. However, above the melting point of these materials, the hydrocarbon block disorders while the fluorocarbon blocks remain rigid. The LAM frequency then results from the longitudinal oscillations of a fluorocarbon end block rather than the entire molecule.

The work described herein was undertaken as an extension of studies on semifluorinated oligomers, with the intent of exploring the effect of a rigid-core unit as opposed to the center semiflexible hydrocarbon block utilized in previous triblock investigations.[8] To this end, a series of symmetrically substituted diperfluoroalkylbenzenes were synthesized and characterized by differential scanning calorimetry and both Fourier transform and conventional Raman spectroscopy. The *p*-bis(perfluoroalkyl)benzenes, $F(CF_2)_nC_6H_4(CF_2)_nF$ with $n = 6, 7, 8, 10$, and 12, hereafter referred to as F*n*PhF*n*, were prepared by copper-mediated condensation of the appropriate perfluoroalkyl iodide with *p*-diiodobenzene in dimethyl sulfoxide. Comparison of the spectra of these oligomers with model compounds allowed assignment of the characteristic Raman-active vibrations of both the para-substituted phenyl ring and the perfluoroalkyl chains. Studies as a function of temperature or pressure revealed the existence of a solid–solid phase transition in F7PhF7, the only oligomer studied that is substituted with perfluorocarbon chains containing an odd number of carbon atoms. Normal-mode calculations, performed for the isolated molecules, were used for comparison to the low-frequency Raman spectral region to assist in understanding the impact of the aromatic core on the LAM vibration.

Experimental Methods

Characterization. Differential scanning calorimetry (DSC) measurements were performed with a Du Pont 1090 thermal analyzer, using a scanning rate of 10 °C/min. All the data reported are the result of second heating experiments in order to remove the effects of any previous processing history that occurred during synthesis.

Proton magnetic resonance spectra were recorded on an IBM Instruments AF250 NMR spectrometer, operating at 250.13 MHz for ^1H at room temperature. Samples were ^2H locked by using the solvent resonance from dimethyl-d_6 sulfoxide and referenced to a residual solvent signal at δ 2.49. The ^{19}F NMR spectra were obtained with an IBM Instruments AF300 NMR spectrometer, operating at 282 MHz for ^{19}F at 80 °C. Samples were ^2H locked by using the solvent resonance from tetrachloroethane-d_2 and referenced to an internal $CFCl_3$. The ^{19}F COSY experiments were carried out in the usual manner. Elemental analysis was performed at Galbraith Laboratories, Knoxville, TN.

Conventional Raman measurements were made with a Jobin-Yvon HG2S double monochromator fitted with a thermoelectrically cooled RCA 31034A-02 photomultiplier tube, standard photon-counting electronics, and a Nicolet 1180 data system. Excitation was provided by a Spectra Physics 165-08 argon ion laser operated at 514.5 nm. Typical spectra were recorded at 2-cm^{-1} resolution by using excitation powers of 300–500 mW. Variable-temperature studies were carried out in a Harney–Miller cell by passing helium gas of the desired temperature over the sample. The sample temperatures reported here were measured with a thermistor placed 2–3 mm from the laser spot on the sample and have a measurement uncertainty of ±3 °C.

Variable-pressure Raman experiments were performed in the backscattering geometry employing a Waspalloy diamond anvil cell with metal gaskets.[9] Pressures were determined in situ from the peak position of fluorescence from added ruby, with an error of ±1 kbar.

The Fourier transform Raman (FT-Raman) spectra were collected on a Bomem DA3.02 interferometer equipped with a thermoelectrically cooled InGaAs detector.[10] Typical excitation powers of 700 mW were provided by the 1.064-μm emission from a Spectron Model SL50 continuous-wave Nd:YAG laser. All FT-Raman spectra were recorded with 4-cm^{-1} resolution.

Synthesis. The synthesis of the 1,4-bis(perfluoroalkyl)benzenes was accomplished by the general method of McLoughlin and Thrower involving the addition of a perfluoroalkyl copper reagent to an aromatic halide.[11] In order to assure complete reaction, excess quantities of both perfluoroalkyl iodide (2.2–2.5 mol equiv) and copper metal (8.0 mol equiv) were used, and the reaction temperature was enhanced somewhat above that usually employed. As the length of the perfluoroalkyl chain was increased, the products gradually became more intractable and difficult to purify and yields were lowered somewhat. It was found that acetic acid was very useful to extract the products from the crude reaction mixtures, which contained copper salts and other byproducts, and this same solvent was very suitable for recrystallization.

The preparation of F8PhF8 illustrates the general method. In a 200-mL pear flask with stirbar and reflux condenser were

0024-9297/91/2224-3901$02.50/0

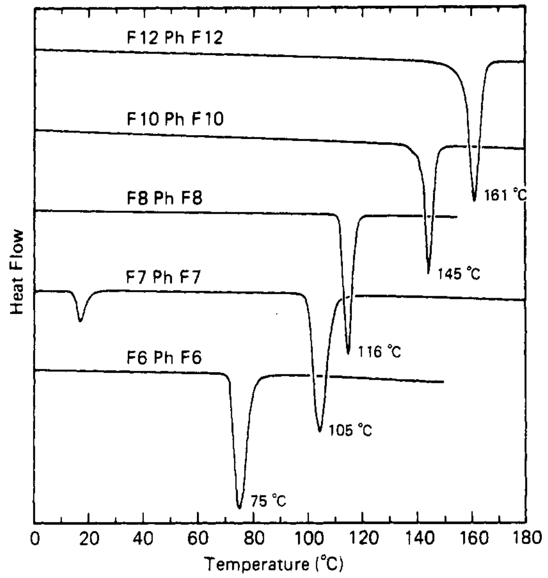

Figure 1. Differential scanning calorimetry thermograms of the FnPhFn triblocks. Temperatures refer to peak positions.

placed 1,4-iodobenzene (3.30 g, 10.0 mmol), 1-iodoperfluorooctane (12.05 g, 22 mmol), anhydrous methyl sulfoxide (25 mL), and copper powder (5.08 g, 80 mmol, 10-μm particle size). The resultant slurry was gradually warmed in an oil bath to 160 °C over 1 h and then maintained at 160 °C for an additional 30 min. After this time thin-layer chromatography indicated all the 1,4-diiodobenzene had been consumed and the slurry was cooled to room temperature and brought up to 200 mL by the dropwise addition of water. The solids were isolated by suction filtration, washed well with water, and then air dried. The solids were transferred to a 500-mL Erlenmeyer flask and boiled with acetic acid (300 mL), and the hot solution was filtered into a second Erlenmeyer flask fitted with stirbar, powder funnel, and filter paper. The contents of the second Erlenmeyer flask were refluxed to rinse out the filter paper, and as the filtrate became concentrated additional hot acetic acid extracts (totalling 600 mL) of the original solids were added. The final filtrate in the second Erlenmeyer flask was concentrated to about 150 mL and cooled with stirring. Suction filtration provided the crude product (8.5 g), which was subsequently hot filtered and recrystallized twice more from acetic acid to provide 6.11 g (66%) of pure product, mp 116 °C: ^{1}H NMR δ 7.79 (s); ^{19}F NMR δ -72.8 (3 F), -102.4 (2 F), 112.5 (2 F), -113.0 to -113.4 (6 F total), -114.1 (2 F), -117.4 (3 F). Anal. Calcd for $C_{22}H_4F_{34}$: C, 28.90; H, 0.44; F, 70.65. Found: C, 28.55; H, 0.38; F, 71.28.

Results and Discussion

Thermal Analysis. Differential scanning calorimetric (DSC) measurements were carried out on the semifluorinated phenyl triblocks, FnPhFn, and the melting endotherms are shown in Figure 1. As expected, the melting points increase as the length of the fluorocarbon end blocks increases. In Figure 2, the melting points are plotted as a function of the total number of backbone carbon atoms so that a comparison with perfluoroalkane oligomers as well as previously studied semifluorinated diblocks and triblocks can be made. The phenyl triblocks form a curve with a shape similar to the perfluoroalkanes, as opposed to the semifluorinated triblocks, which exhibit behavior intermediate between perfluorocarbons and pure hydrocarbons. Interestingly enough, it can be concluded that the effect of the phenyl group is to lower the melting point of the FnPhFn compounds relative to their perfluoroalkane counterparts, hence acting like a defect in the lattice.

The compound F7PhF7, the only member of the series that is formed from fluorocarbon chains containing an odd number of carbon atoms, displays an anomalously higher melting temperature as well as a weaker endotherm at 17 °C, as shown in Figure 1. This lower temperature endotherm is characteristic of a solid–solid phase transition and is not observed in the even carbon number members of the series. The unavailability of other odd oligomers prevents investigation of the generality of this odd–even difference on the thermal behavior, but the Raman spectra for this compound will be used to corroborate the presence of a different structure for F7PhF7.

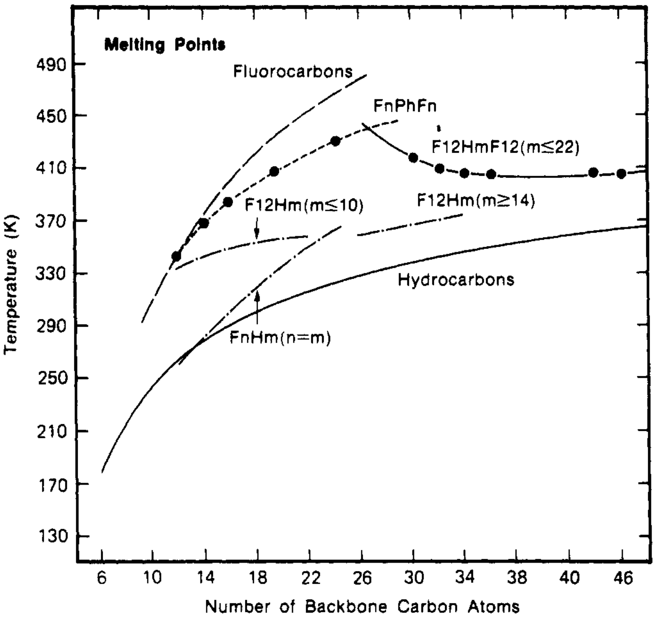

Figure 2. Comparison of the melting points of the FnPhFn triblocks with those of the n-alkanes, perfluoro-n-alkanes, and previously studied diblock and triblock materials.

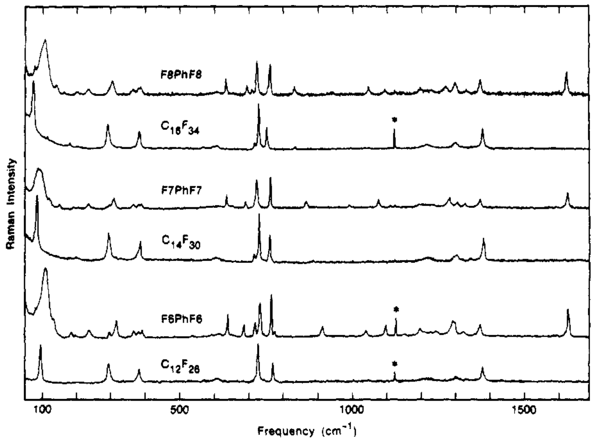

Figure 3. Conventional Raman spectra of three FnPhFn triblocks compared to the perfluoro-n-alkane analogues of the same total fluorocarbon chain length, allowing vibrational assignments. Those bands arising from the phenyl ring are clearly absent in the pure fluorocarbon spectra, e.g., the aromatic C═C stretch at 1625 cm^{-1} (see text). The band appearing with varying intensity near 1125 cm^{-1} in all conventional Raman spectra shown here is a spurious emission line due to room light.

Raman Measurements. In order to make assignments of those vibrational bands characteristic of the aromatic core of the FnPhFn compounds, a comparison of the conventional Raman spectra of the semifluorinated phenyl triblocks with perfluoro-n-alkanes of the same total fluorocarbon chain length is made in Figure 3. The C═C stretch of the phenyl ring at 1625 cm^{-1} is clearly absent in the pure fluorocarbon spectra. Similarly, localized vibrations of the ring at 1095, 695, and 635 cm^{-1} are conclusively marked by their absence in the perfluoroalkane spectra and their insensitivity to chain length. Other

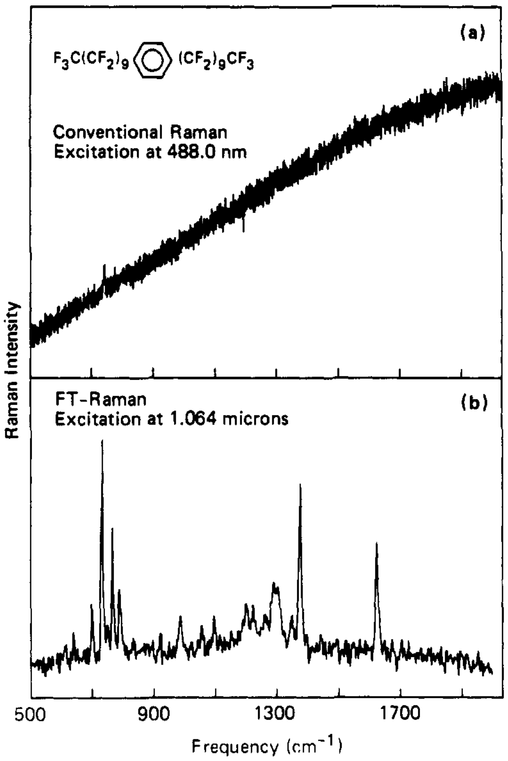

Figure 4. Impurity fluorescence preventing measurement of the conventional Raman spectra of the longer chain members of the FnPhFn series (a). Near-infrared wavelength excitation preventing impurity absorption and subsequent fluorescence and allowing collection of the FT-Raman spectrum (b).

bands in the spectral region shown are significantly correlated with bands in the perfluoroalkane spectra. Sharp bands between 700 and 750 cm^{-1} and weaker modes between 300 and 400 cm^{-1} are attributable to various $-CF_2$ vibrations. In the region from 800 to 1400 cm^{-1} a number of bands are observed whose frequencies change with chain length. These bands could be used to map out portions of the phonon dispersion curves for the polymer, as has been shown for the n-alkanes[12] and perfluoro-n-alkanes.[13]

Conventional Raman spectra can be quite difficult to acquire for these FnPhFn compounds due to fluorescence arising from impurities, which, as mentioned in the description of their preparation, are increasingly difficult to remove as n increases. Routine photobleaching for many hours was required prior to recording the conventional spectra shown here, and insufficient removal of fluorescence by this process accounts for differences in signal-to-noise ratio in the spectra, especially for longer chain lengths and at low temperatures. Spectra for the longer compounds, F10PhF10 and F12PhF12, were almost impossible to measure with conventional visible excitation, as shown in the upper portion of Figure 4. However, by avoidance of the electronic absorption which precedes fluorescence, via excitation in the near infrared at 1.064 μm, the FT-Raman spectrum shown in the lower portion of Figure 4 could be obtained. In Figure 5 the FT-Raman spectra for the entire series of FnPhFn compounds are shown. Comparison of the conventional spectra of the shorter members of the series (Figure 2) with their FT analogues in Figure 5 reveals essentially identical spectra. Thus, the FT approach provides a means to extend the investigation to the longer chain length compounds, which could not be investigated by using conventional Raman spectroscopy.

The low-frequency region of the Raman spectrum (<200 cm^{-1}) of the perfluoro-n-alkanes shown in Figure 3 displays an intense sharp band whose frequency is inversely proportional to chain length.[1] This longitudinal acoustic mode (LAM) is an accordion-like vibration of the extended chain. For the diblock and triblock systems studied previously, where the fluorocarbon chains were covalently bonded to a semiflexible linear hydrocarbon chain, it was found that coupling between the fluorocarbon and hydrocarbon chains occurred in the solid state, giving rise to a LAM mode in the low-frequency spectra characteristic of the entire FnPhFn molecule. The question to be addressed in the present study is whether substitution of the semiflexible hydrocarbon block with the very rigid aromatic core decouples the two fluorocarbon chains from one another. As Figure 3 shows, the LAM vibrations for the perfluoro-n-alkanes of appropriate length occur just below 100 cm^{-1}. However, as observed for the phenyl triblocks, this region is dominated by an intense but rather broad band near 100 cm^{-1}, which displays no systematic correlation of frequency with chain length and therefore does not originate from a LAM-like vibration. In addition, none of the other low-intensity bands in the region between 50 and 200 cm^{-1} exhibit the inverse dependence of frequency on chain length, which is characteristic of LAM.

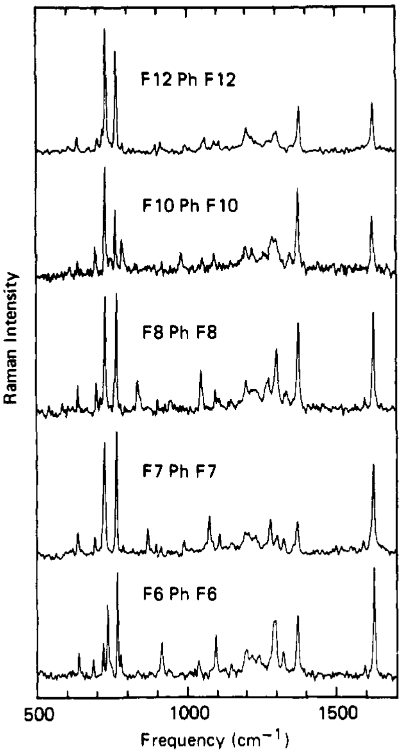

Figure 5. FT-Raman spectra recorded for all members of the FnPhFn series. Conventional Raman spectra can be measured only for the three compounds of shorter chain length (see Figure 3 for comparison).

Raman measurements at low temperature are shown in Figure 6. For all three compounds, bands above 200 cm^{-1} are observed to narrow at low temperature, as might be expected when molecular motion is reduced. By far the most notable change involves the broad intense band near 100 cm^{-1} for the F7PhF7 oligomer, whose position shifts by about 30 cm^{-1} to higher frequency. Although this band also shifts in F6PhF6 and F8PhF8, in those cases the shifts are only about 10 cm^{-1} and the mode is observed to move up in frequency for F6PhF6 as the temperature is decreased, while moving down in frequency for F8PhF8. Since this band is not present in the perfluoro-n-alkanes, its origin is connected to the insertion of the aromatic core into the fluorocarbon chain. At such low frequency, it seems reasonable to expect that this band represents a

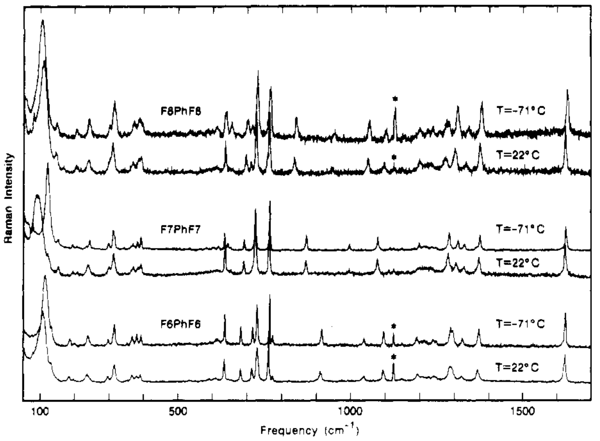

Figure 6. Conventional Raman spectra of the three shorter chain F*n*PhF*n* compounds at room temperature and at low temperature. The low-frequency region (<200 cm^{-1}) does not reveal any band that can be correlated with LAM-1 but is dominated by an intense broad, temperature-sensitive band near 100 cm^{-1}.

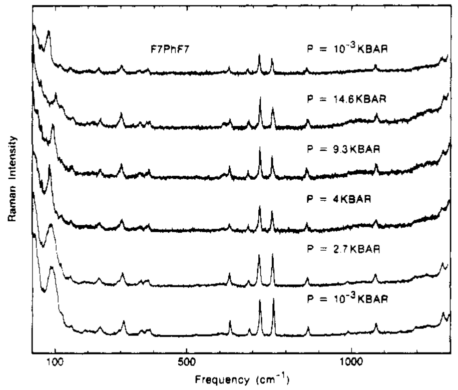

Figure 7. Variable-pressure Raman measurements of the F7PhF7 oligomer. A phase transition involving conversion of the helical fluorocarbon chains to a planar zigzag conformation is marked by the appearance of the 625-cm^{-1} band at 9 kbar.

low-energy vibration involving the ring, perhaps a libration of the ring within the fluorocarbon chain. As shown in Figure 1, F7PhF7 is the only compound studied that exhibits a solid–solid phase-transition endotherm, and the significantly different behavior of the low-frequency mode near 100 cm^{-1} for this compound can be correlated with changes in the intermolecular packing of the oligomeric molecules with a subsequent change in the intermolecular environment around the ring.

In order to assess the feasibility of such an interpretation, variable-pressure Raman measurements were made to explore the possibility of differences in molecular packing or conformation for the F7PhF7 oligomer compared to its even carbon number chain analogues. The Raman spectrum of F7PhF7 as a function of pressure, shown in Figure 7, discloses two major changes. At a pressure near 4 kbar the low-frequency band in question narrows and moves to lower frequency, suggesting a restriction of the motion involved in this mode. At 9 kbar, a new band appears at 625 cm^{-1}, which has previously been assigned to the planar zigzag form of fluorocarbon chains,[14] in contrast to the helical conformation characteristic of the ambient pressure phase. Accompanying the conformational change of the fluorocarbon side chains, the low-frequency band at 100 cm^{-1} reverses its intermediate behavior by again broadening and returning to a higher frequency position. At the even higher pressure of 14.6 kbar, the low-frequency mode is substantially reduced in intensity, suggesting that the motional freedom that characterizes this mode is decreasing. Lowering the applied pressure results in recovery of the ambient spectrum.

The lack of any Raman bands between 50 and 200 cm^{-1} that display the chain-length-dependent behavior characteristic of LAM suggests that insertion of the rigid aromatic core into the fluorocarbon chain has significantly changed the delocalized vibrations of the molecule. Of course, insertion of the phenyl group might lead to a change in the fluorocarbon chain conformation, which would also be expected to influence LAM behavior. However, recent experiments with perfluorocarbon oligomers have explored the effect of pressure-induced conformational changes on LAM,[15] revealing that a negative shift in the LAM frequency of only 14 cm^{-1} occurs when C_7F_{16} changes from its usual helical form to a planar zigzag conformation. Thus, the absence of LAM bands for F*n*PhF*n* must be correlated with effects of the aromatic core other than simple chain conformational changes. Coupling of the two fluorocarbon chains through the rigid ring should produce a LAM vibration with a frequency near that expected for the total chain length of $F(CF_2)_{2n}F$. For example, if vibrational coupling through the ring were possible, F8PhF8 should display a LAM frequency near that of $C_{16}F_{34}$, which occurs at 74 cm^{-1}, while the F7PhF7 and F6PhF6 LAM should appear at 84 and 95 cm^{-1}, respectively. If the ring decouples the vibrations of the two fluorocarbon chains but individual LAM vibrations of the independent chains are possible, then the LAM frequency would occur near that of C_8F_{18} at 135 cm^{-1} or of C_7F_{16} at 146 cm^{-1}. (Of course, one end of the chain is now attached to the phenyl ring, which would be expected to produce slight negative frequency shifts for the LAM mode due to simple mass effects.) Bands with this behavior are not apparent in the spectra, although the presence of the low-frequency ring mode near 100 cm^{-1} might contain some component of accordion-like motion. Normal-mode calculations were initiated in order to address these questions about LAM.

Normal-Mode Calculations. Normal-mode calculations were performed to investigate the effect of a rigid core on the LAM in triblock semifluorinated carbon chains. The skeletal approximation[12] was used for an isolated chain assuming either a planar zigzag or 15/7 helical conformation. CF_2 groups along the fluorocarbon chains as well as the CH members of the phenyl ring were treated as single points of appropriate mass. This approximation is known to have only minor effects on the calculated LAM frequency for the *n*-paraffins[12] and semifluorinated *n*-alkanes.[8] The force field utilized in these numerical studies, given in Table I, includes force constants for CC stretches, CCC bends, and near-neighbor interactions of the fluorocarbon chains similar to those used previously.[8] Force constants for the ring were taken from a simplified force field determined for the alkylbenzenes.[13]

Simple physical models for the F*n*PhF*n* compounds indicate two possible conformations of the chains with respect to the central ring. One conformation involves the two chains in an effective trans attachment to the ring, so that the two fluorocarbon chains are aligned parallel but not collinear to one another. The plane of the ring is tilted relative to the fluorocarbon chain axes and displaces the two chains from a linear conformation. The second conformation is a cis attachment of the chains to the ring, so that the two chains are no longer parallel but form a "V" shape with an interior angle of approximately 140°. While these two "most likely" configurations were obtained after consideration of space-filling models, other artificial conformations were also investigated to ascertain the effect of the nonlinearity induced by inclusion of the

Table I
Valence Force Field Used for the Calculation of Low-Frequency Motions in F*n*PhF*n* Molecules[a]

force constant	value
Ring In-Plane	
CC stretch (T)	6.4153
CCC bend (Ω)	1.0284
CC stretch ring-chain (R)	4.6813
CCC bend ring-chain (Φ)	0.7535
CC,CC stretch–stretch interaction ($T_{i,i+1}$)	0.7716
CC,CC stretch–stretch interaction ($T_{i,i+2}$)	−0.3189
CC,CC stretch–stretch interaction ($T_{i,i+3}$)	0.2895
CC,CC stretch–stretch interaction (T,R)	0.2506
CC,CCC stretch–bend interaction (T,Ω)	0.1187
CC,CCC stretch–bend interaction (T,Φ)	0.186
CC,CCC stretch–bend interaction (R,Φ)	0.5415
Ring Out-of-Plane	
CCCC torsion ring-chain (τ)	0.0001
Fluorocarbon Chains	
CC stretch	3.963
CCC bend	0.942
CC,CC stretch–stretch interaction	0.148
CC,CCC stretch–bend interaction	0.166
CCC,CCC bend–bend interaction	0.492
CCCC torsion	0.149

[a] Values and notation of force constants for the phenyl ring are taken from ref 13; force constants for the fluorocarbon chains are taken from ref 8.

ring into the fluorocarbon chain. These nonphysical conformations force the plane of the ring to lie along the axis of the fluorocarbon chains.

The LAM vibration has been shown to involve an accordion-like oscillation of the carbon atoms solely along the long axis (z axis) of the chain. Since Raman scattering intensity is proportional to the square of the polarizability induced by a vibration, only LAM modes with an odd number of nodes in atomic displacement along the z-axis can be Raman active. By plotting the atomic displacements, it is possible to determine those normal modes that correspond to LAM-k modes, where k is an integer denoting the number of nodes along the z axis. For the artificial conformation, which forces the ring to remain coplanar with both all-trans chain axes, the LAM-1 is essentially unperturbed from that of the fluorocarbon chain with the same number of CF_2 groups but no internal phenyl ring. If the ring is coaxial with the chains, but the plane of the ring is orthogonal to the planes of the carbon chains, the intensity of LAM-1, as measured by the magnitude of the z-displacements, decreases while the atomic motions perpendicular to the chain axis increase. The magnitudes of the atomic displacements orthogonal to the chain axes continue to increase at the expense of the z-displacements when the ring is tilted with respect to the chain segments. Similar behavior has been observed upon insertion of a C=C bond into an alkane chain in a trans conformation.[16] Not only does the intensity of the LAM-1 band for the phenyl triblocks decrease significantly but the frequency decreases by as much as 50 cm^{-1}. These two observations effectively corroborate the experimental measurements: no LAM is observed for the phenyl triblocks because the nonplanarity introduced by the central aromatic substitution causes a severe loss of intensity as well as a depression of the vibrational frequency.

Conclusions

The effect of a stiff phenyl unit on cooperative motion between fluorocarbon segments has been investigated in a series of FnPhFn (n = 6, 7, 8, 10, and 12) compounds. Raman studies in the low-frequency region revealed the presence of a broad, intense band at ~100 cm^{-1} whose position did not vary significantly with chain length but did show a different variation with temperature for F7PhF7 compared to the other oligomers studied. DSC studies revealed the presence of a low-temperature phase transition in this material, suggesting that its low-temperature crystal structure was similar to that of its longer chain analogues at room temperature. Spectroscopic measurements indicate that, as the F7PhF7 is heated above its transition, it enters an intermediate state of unknown crystal structure before melting. High-pressure studies were initiated to further elucidate the nature of this intermediate state and its effect on the 100-cm^{-1} band. It was concluded that this band could be attributed to librational motions of the phenyl ring, which could be shown to change dramatically in a high-pressure environment. Hence, this intense low-frequency vibration cannot be attributed to a LAM. Normal-mode calculations in the isolated chain and point mass approximations were undertaken, and the results are consistent with this interpretation.

Acknowledgment. We thank R. L. Siemens for his assistance with the thermal analysis and W. Fleming, R. Johnson, and O. Nguyen for the NMR determinations. We also acknowledge the financial support and technical motivation of L. Siperko and D. Barr of the IBM Endicott Laboratories.

References and Notes

(1) Rabolt, J. F.; Fanconi, B. *Macromolecules* **1978**, *11*, 740.
(2) Masetti, G.; Cabassi, F.; Morelli, G.; Zerbi, G. *Macromolecules* **1973**, *6*, 700.
(3) Hannon, M. J.; Boerio, F. J.; Koenig, J. L. *J. Chem. Phys.* **1969**, *50*, 2829.
(4) Twieg, R.; Rabolt, J. F. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 901.
(5) Minoni, G.; Zerbi, G. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 533.
(6) Rabolt, J. F.; Russell, T. P.; Twieg, R. J. *Macromolecules* **1984**, *17*, 2786.
(7) Russell, T. P.; Rabolt, J. F.; Twieg, R. J.; Siemens, R. L.; Farmer, B. L. *Macromolecules* **1986**, *19*, 1135.
(8) Twieg, R. J.; Rabolt, J. F. *Macromolecules* **1988**, *21*, 1806.
(9) Rabolt, J. F.; Piermarini, G.; Block, S. *J. Chem. Phys.* **1978**, *69*, 2872.
(10) Zimba, C. G.; Hallmark, V. M.; Swalen, J. D.; Rabolt, J. F. *Appl. Spectrosc.* **1987**, *41*, 721.
(11) McLoughlin, V. C. R.; Thrower, J. *Tetrahedron* **1969**, *2*, 5921.
(12) Shimanouchi, T.; Tasumi, M. *Indian J. Pure Appl. Phys.* **1971**, *9*, 958.
(13) LaLau, C.; Snyder, R. G. *Spectrochim. Acta* **1971**, *27A*, 2073.
(14) Wu, C. K.; Nicol, M. *Chem. Phys. Lett.* **1973**, *21*, 153.
(15) Song, K.; Hallmark, V. M.; Rabolt, J. F. *J. Chem. Phys.*, in press.
(16) Rabolt, J. F.; Twieg, R. J.; Snyder, C. *J. Chem. Phys.* **1982**, *76*, 1646.

Registry No. F6PhF6, 124389-30-6; F7PhF7, 132877-70-4; F8PhF8, 132877-69-1; F10PhF10, 132877-68-0; 1,4-diiodobenzene, 624-38-4; iodoperfluorooctane, 507-63-1.