and slowly evaporated. In the case of R4DB (M_w 50 000) no change in η_0 was observed. It is concluded that the observed melt viscosities of the lightly entangled rings ($MW < 10^5$) are probably true values. R19D was treated similarly. When the polymer content reached 90%, the sample was placed for 3 h at 150 °C in a pressure vessel in a benzene atmosphere. All residual benzene was removed under vacuum at room temperature. After this treatment the melt viscosity of R19D increased by a factor of 2 (arrow in Figure 3) and $(G_N{}^\circ)_r$ had risen from $0.5(G_N{}^\circ)_l$ to $0.7(G_N{}^\circ)_l$. Unfortunately, the ultracentrifuge pattern of the sample indicated that some degradation had occurred during the treatment and subsequent measurements (30% linear polymer with the same molecular weight as the ring and 20% low molecular weight material). Nevertheless, the increased melt viscosity indicates that the increased entanglement of the rings outweighs the effects of low molecular weight linear material in the sample. Of course, it is not established that in the limit $(G_N{}^\circ)_r = (G_N{}^\circ)_l$.

Ring polymers with $MW > (M_c)_l/g_r \approx 7 \times 10^4$ are expected to be effectively entangled. However, because of the low values of $(G_N{}^\circ)_r$ the measured viscosities of the large entangled rings are probably only minimum values that differ increasingly from the true η_0 as the molecular weight increases. For the same reason, the values of the recoverable compliance $J_e{}^\circ$ of the rings ($J_e{}^\circ = 1/\eta_0{}^2 \lim_{\omega\to 0} (G'/\omega^2)$ given in Table I are probably only apparent. Note, however, that for the lowest molecular weight ring $J_e{}^\circ \approx {}^1/_2(J_e{}^\circ)_l$, in accord with the Rouse model.[4]

In conclusion, it can be said that the observed melt viscosities are minimum values which show enhanced η_0 over linear polymers of the same *size*. Therefore, these data provide partial indirect evidence for the tube model and reptation.

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Registry No. Polystyrene (homopolymer), 9003-53-6.

References and Notes

(1) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.
(2) Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(3) Dodgson, K.; Bannister, D. J.; Semlyen, J. A. *Polymer* **1980**, *21*, 663.
(4) Bloomfield, V.; Zimm, B. *J. Chem. Phys.* **1966**, *44*, 315.
(5) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(6) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(7) Onogi, S.; Masuda, T.; Kitagawa, K. *Macromolecules* **1970**, *3*, 109.
(8) Plazek, D. J.; O'Rourke, V. M. *J. Polym. Sci., Part A-2* **1971**, *9*, 209.
(9) McKenna, G. B. *Symp. Faraday Soc.* **1983**, *18*, 210–11, 245–6.
(10) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959; **1981**, *14*, 766.
(11) Roovers, J. *Macromolecules* **1984**, *17*, 1196.
(12) Masuda, T.; Ohta, Y.; Yamaguchi, T.; Onogi, S. *Polym. J.* **1984**, *16*, 273.
(13) Antonietti, M.; Coutandin, J.; Grütter, R.; Sillescu, H. *Macromolecules* **1984**, *17*, 798.
(14) Plazek, D. J.; Raghupathi, N.; O'Rourke, V. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1837.

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Observations of a "Gel" Phase in Binary Mixtures of Semifluorinated *n*-Alkanes with Hydrocarbon Liquids

Semifluorinated *n*-alkanes, $F(CF_2)_n(CH_2)_mH$ (F*n*H*m* in our notation) have been the subject of a number of recent studies in both the melt[1] and solid state.[2-4] Results indicate that only partial disordering of the molecular chain occurs in the melt, with a partial ordering maintained in the fluorocarbon portion of the molecule. When these materials crystallize, several different morphologies result,[2] depending on the fluorocarbon-to-hydrocarbon ratio (n/m) in the molecule.

An investigation of binary mixtures of semifluorinated *n*-alkanes in hydrocarbon liquids has revealed[5] the existence of a new phase which exhibits gel-like characteristics and henceforth will be referred to as a "gel". This phase results when a mixture of an F*n*H*m* compound and various hydrocarbon liquids (see Tables I and II) is heated above the melting point of the corresponding F*n*H*m* to form a homogeneous fluid and then allowed to cool to room temperature. Once the gel is formed, the transition between the gel phase and an isotropic, transparent fluid is reversible. The temperature, T_c, at which this transition occurs and the opacity of the gel phase depend upon the concentration of the components in the mixture. This transition temperature above which the mixture is visibly transparent also corresponds (±2 °C) to an endotherm easily measured by differential scanning calorimetry (DSC). However, in comparison to the melting endotherm observed for the neat F*n*H*m*, the endotherm of the gel transition is broad (extending over some 40 °C compared to 10 °C for the solid) and skewed toward the low-temperature side, indicating that a gradual disordering occurs over this range prior to the temperature of the endotherm minimum. In addition, the enthalpies (per mole of F*n*H*m*) of the observed gel transitions have been found to be consistently larger than that found for the melting of the pure solid.

Macroscopically the "gel" phase is manifested by an extremely large zero-shear viscosity, which reverts to that of a low-viscosity liquid upon heating above T_c. When this "gel" phase was vigorously shaken it remained intact. In fact, it could also be inverted in a tube and left for several days without any noticeable flow. Microscopically the gel was observed to exhibit birefringence between crossed polarizers which disappeared above T_c. Under high magnification the presence of what appeared to be a microfibrillar morphology was also noted.

Table I
F*n*H*m* + Decane

n	*m*	gel formed
12	2	no
12	4	no
12	6	marginal
12	8–20	yes
14	0	no

Table II
F10H12 + Solvent

solvent	gel formed	solvent	gel formed
octane	yes	perfluorooctane	no
decane	yes	cyclodecane	yes
dodecane	yes	caprylic acid	yes
tetradecane	yes	PEO-400	no
hexadecane	yes	2-methylnonadecane	yes
perfluorocyclohexane	no	decalin	yes

0024-9297/85/2218-1361$01.50/0

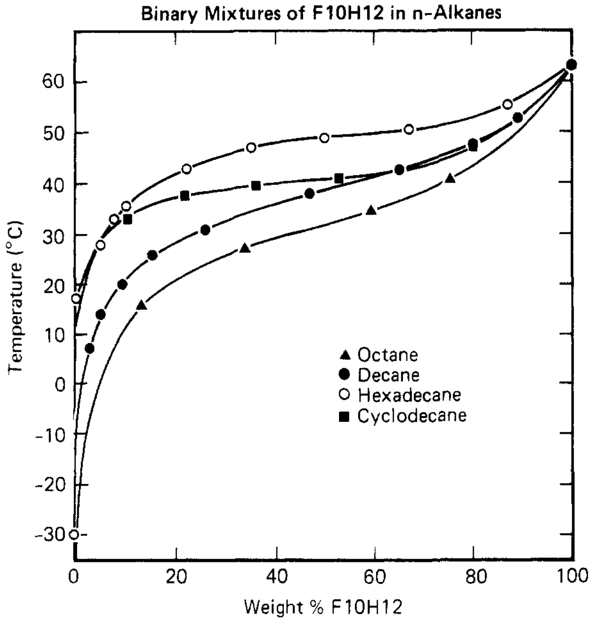

Figure 1. Phase diagrams of F10H12 in octane, decane, hexadecane, and cyclodecane. Transition temperature corresponds to the endotherm minimum obtained from differential scanning calorimetry measurements in a sealed sample pan. Sample weights were checked before and after heating cycles in order to ensure that no loss of sample occurred.

Shown in Figure 1 are phase diagrams which have been determined through a series of DSC measurements on F10H12 in *n*-octane, *n*-decane, *n*-hexadecane, and cyclodecane. There is a clear dependence on concentration of F10H12 (weight percent) which affects the transition temperature, T_c, where the opaque, viscous gel transforms into a low-viscosity transparent fluid.

It is interesting to note the shape of these phase diagrams and how they vary with the nature of the cosolvent. At high concentrations, a linear portion of the curve is observed and is similar to what would be expected for a simple melting point depression. At intermediate concentrations (<90%) the positive curvature toward higher temperatures reflects the intermolecular interaction between F10H12 and the alkane, indicating that the gel disorders at a temperature much higher than would be expected from a depression of the melting point of F10H12 due simply to concentration. The fact that this interaction is dependent on the nature of the cosolvent is exemplified by the change in shape of the phase diagram in going from linear to cyclic alkanes. This suggests that the interaction parameter may be sensitive to the shape of the cosolvent molecules as dictated by the allowable conformations.

These results taken collectively strongly suggest that the structure of the gel phase is considerably different from that of the solid state. In fact, preliminary wide-angle X-ray diffraction measurements (WAXD) revealed that in a gel of F10H12/hexadecane, many of the strong intersegmental *d* spacings increase above that of the neat solid, while others disappear. An extensive systematic study (including WAXD, SAXS, IR spectroscopy, and Raman spectroscopy) has been undertaken to determine the precise structure of this gel phase, and the results will be the subject of a future publication.[6]

Registry No. F10H12, 93454-71-8.

References and Notes

(1) Twieg, R.; Rabolt, J. F. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 901.
(2) Rabolt, J. F.; Russell, T.; Twieg, R. *Macromolecules* **1984**, *17*, 2786.
(3) Minoni, G.; Zerbi, G. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 533.
(4) Mahler, W. *Macromolecules*, submitted.
(5) Mahler has observed formation of "gel" phases on cooling hydrocarbon solutions of partially fluorinated alkanes (W. Mahler, DuPont, private communication).
(6) Twieg, R.; Russell, T. P.; Siemens, R.; Rabolt, J. F., to be published.

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