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Communication

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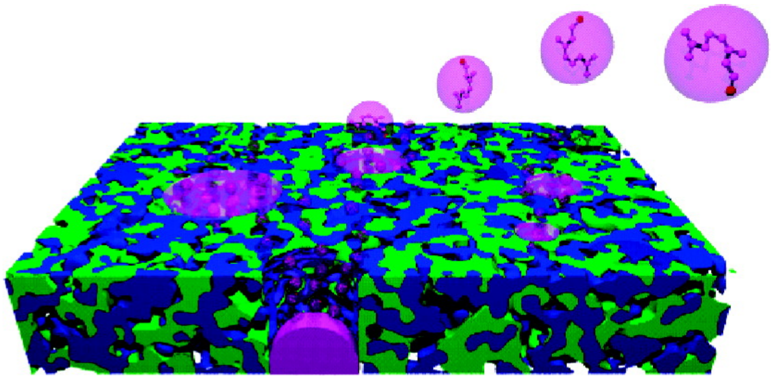

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Unusual, Promoted Release of Guests from Amphiphilic Cross-Linked Polymer Networks

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The packaging and release of guests from nanoscopic hosts is an area of active research that holds promise in controlled delivery applications. Peppas has developed a number of novel polymeric systems for controlled and targeted drug delivery and has studied extensively the diffusion of small molecules in these systems.[1,2] In such systems, the ability to control the path length of the diffusing guests (e.g., by creating increasing path lengths with increasing crystallite size)[3,4] provides for alteration in the uptake and release properties. Liu and co-workers have created thin membranes containing hexagonally packed and uniformly sized nanochannels that behave as “chemical valves”, which have demonstrated potential as drug delivery candidates.[5] The self-assembly of di- and triblock copolymers into a wide array of unique nanoscale morphologies is now a well-known method to create interesting materials,[6] which, for example, has been used as thin film templates and scaffolds for the fabrication of flash memory devices.[7] Our interest is in the study of robust composite polymer systems as hosts for volatile guests in numerous applications and in the preparation of the host system having nanoscale differential domains produced by the in situ cross-linking of incompatible polymer components as they undergo phase segregation.

Amphiphilic and morphologically complex nanostructured materials were designed as novel hosts for the packaging, partitioning, and release of volatile guests and guest mixtures. These materials were prepared by cross-linking in situ phase segregating mixtures of a hydrophobic hyperbranched fluoropolymer (HBFP) and a hydrophilic poly(ethylene glycol) diamine (PEG) via reaction of the terminal amines of the PEG component with the labile para positions of the pentafluorophenyl chain ends of HBFP (Figure 1).[8,9]

Characterization of the subsurface nanoscale features of the HBFP−PEG cross-linked networks was performed using transmission electron microscopy (TEM). For example, the TEM images in Figure 2 show the selective staining of PEG-rich domains with ruthenium tetroxide,[10−12] in contrast to the HBFP-rich domains stained selectively with osmium tetroxide.[13] These network polymers having complex surfaces and morphologies exhibited high loading capacities but also unusually rapid kinetics for the release of guests of hydrophobic, hydrophilic, or amphiphilic character.

Thermogravimetric analysis (TGA) was utilized as a sensitive and convenient technique to monitor the thermodynamics and kinetics of the terpene geraniol as a volatile guest undergoing uptake within and release from from HBFP−PEG cross-linked networks of varying compositions.

Figure 3 displays the TGA and DTGA (first derivative of TGA curve with respect to time) curves for geraniol-loaded (45−60 wt %) HBFP, PEG, and HBFP−PEG cross-linked networks. The TGA profile for each geraniol-loaded material exhibited two distinct mass loss regions. The first region, ca. 100−200 °C, corresponds to the loss of geraniol from the polymer network and the second region, above 300 °C, to the decomposition of the polymer.[14] The temperature at which half mass loss of geraniol occurred (peak minimum observed in the DTGA curve) from these samples is defined as T_{50}^{Dynamic}.[15]

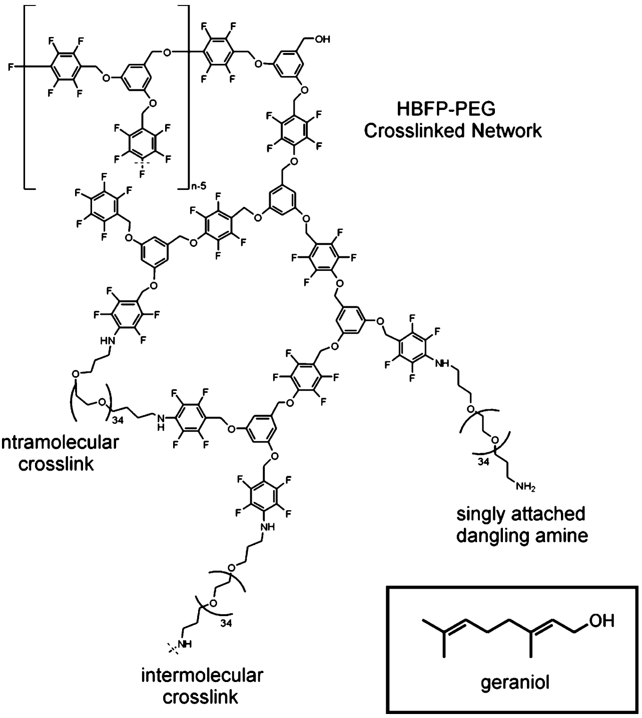

Figure 1. Structures of HBFP−PEG hosts and geraniol guest.

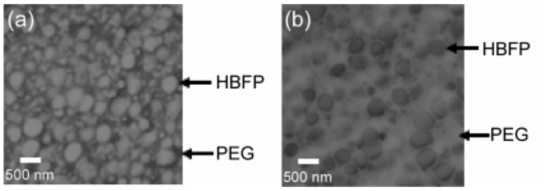

Figure 2. TEM images of an ultramicrotomed HBFP−PEG29 (29 wt % PEG/HBFP) cross-linked network film (ca. 80-nm thickness) stained with ruthenium tetroxide (a) and osmium tetroxide (b) vapors for 20 min.

The T_{50}^{Dynamic} was dependent upon the composition of the host material (Figures 3 and 4). Only small depressions in the geraniol T_{50}^{Dynamic} were observed in the bulk homopolymer samples, whereas significant depressions in T_{50}^{Dynamic} occurred upon sequestration within HBFP−PEG cross-linked networks. From bulk PEG, the magnitude of T_{50}^{Dynamic} decreased linearly with decreasing wt % PEG−HBFP within the cross-linked networks, reaching a minimum

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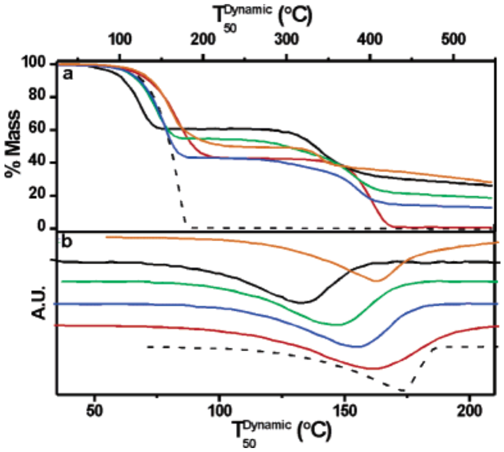

Figure 3. TGA profiles (a) and their corresponding DTGA curves (b) for HBFP−PEG29 (black line), HBFP−PEG45 (green), HBFP−PEG55 (blue), HBFP (orange), and PEG (red) loaded with 45−60 wt % geraniol. The data for neat geraniol (black dashed line) are also included.

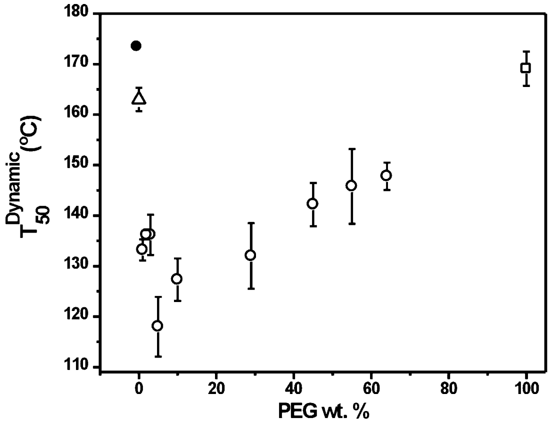

Figure 4. Plot of $T_{50}^{Dynamic}$ of geraniol in HBFP−PEG cross-linked networks (○) of varying wt % PEG/HBFP. The $T_{50}^{Dynamic}$ values for geraniol in both HBFP (△) and PEG (□) as well as the neat liquid (●) are also included.

at 5 wt % PEG−HBFP, and undergoing a subsequent increase in $T_{50}^{Dynamic}$ for cross-linked networks of 3, 2, and 1 wt % PEG−HBFP.

Kinetic data from isothermal (75 °C) TGA studies (see Supporting Information) for the release of geraniol are summarized in Table 1. The release data fit well to first-order kinetics, and from these data, the first-order rate constants (k) and t_{50}^{iso} (amount of time required for half mass loss of geraniol) values were calculated. The first-order rate constants increased, and the t_{50}^{iso} values decreased for the volatilization of geraniol from HBFP−PEG cross-linked networks, each by 1 order of magnitude when compared to neat HBFP or PEG. In agreement with the dynamic TGA observations, the k and t_{50}^{iso} values increased and decreased, respectively, with decreasing wt % PEG relative to neat PEG.

Table 1. First-Order Rate Constants (k) and Time at Half Mass Loss (t_{50}^{iso}) Values for Thermally Promoted Release of Geraniol from HBFP−PEG Cross-Linked Networks at 75 °C

network polymer	PEG wt %	*t_{50}^{iso} (s × 10^{-3})	k (s^{-1} × 10^5)
HBFP	0	22.0 ± 0.2	3.1 ± 0.3
HBFP−PEG10	10	2.2 ± 0.3	31.4 ± 0.2
HBFP−PEG29	29	3.1 ± 0.2	22.6 ± 0.3
HBFP−PEG55	55	3.8 ± 0.7	18.2 ± 0.1
PEG	100	18.0 ± 0.2	3.9 ± 0.4
−	neat geraniol	24.0 ± 0.2	2.9 ± 0.3

*t_{50}^{iso} is the amount of time required for loss of geraniol 50% mass.

We have demonstrated via the use of dynamic and isothermal TGA studies the ability of HBFP−PEG cross-linked networks to sequester significant quantities of geraniol and yet also promote its release as a volatile compound. These results are contrary to common encapsulation/release systems such as cyclodextrins[16,17] and zeolites,[18] which commonly inhibit release, due to favorable interactions within the host matrix. However, precedence for such behaviors does exist for porous inorganic substrates (zeolites and diatomaceous earth) loaded with thermally stable volatile compounds,[19,20] although not with the remarkable temperature depressions or rate enhancements observed for the HBFP−PEG amphiphilic, morphologically complex nanostructured networks. We are currently investigating the roles played by each parameter of the cross-linked network structure, the morphology, and the interfacial interactions, toward the onset of this interesting phenomenon, and expanding the study to a broader range of volatile guest molecules.

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Supporting Information Available: TGA thermograms, isothermal TGA kinetic plots, and a detailed Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Lopez, J. E.; Peppas, N. A. *J. Biomater. Sci., Polym. Ed.* **2004**, *15*, 385.
(2) Robinson, D. N.; Peppas, N. A. *Macromolecules* **2002**, *35*, 3668.
(3) Harland, R. S.; Peppas, N. A. *Colloid Polym. Sci.* **1989**, *267*, 218.
(4) Peterlin, A. *J. Macromol. Sci., Part B* **1975**, *11*, 57−87.
(5) Liu, G.; Ding, J.; Hashimoto, T.; Kimishima, K.; Winnik, F. M.; Nigam, S. *Chem. Mater.* **1999**, *11*, 2233.
(6) Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, *52*, 32.
(7) Xu, T.; Stevens, J.; Villa, J. A.; Goldbach, J. T.; Guarini, K. W.; Black, C. T.; Hawker, C. J.; Russell, T. P. *Adv. Funct. Mater.* **2003**, *13*, 698.
(8) Gan, D.; Mueller, A.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3531.
(9) Gudipati, C. S.; Greenlief, C. M.; Johnson, J. A.; Prayongpan, P.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6193.
(10) Djerassi, C.; Engle, R. R. *J. Am. Chem. Soc.* **1953**, *75*, 3830.
(11) Berkowitz, L. M.; Rylander, P. N. *J. Am. Chem. Soc.* **1958**, *80*, 6682.
(12) Trent, J. S.; Scheinbeim, J. I.; Couchman, P. R. *Macromolecules* **1983**, *16*, 589.
(13) Sawyer, L. C.; Grubb, D. T. *Polymer Microscopy*; Chapman and Hall: New York, 1987.
(14) TGA for cross-linked HBFP−PEG networks, PEG and HBFP indicated that these materials are stable up to 300 °C (see Supporting Information).
(15) Stipanovic, A. J.; Hennessy, P. J.; Webster, F. X.; Takahashi, Y. *J. Agric. Food Chem.* **2004**, *52*, 2301.
(16) Uekama, K.; Hirayama, F.; Esaki, K.; Inoue, M. *Chem. Pharm. Bull.* **1979**, *27*, 76.
(17) Trinh, T. In *Proceedings of the Eighth International Symposium on Cyclodextrins*; Budapest, Hungary, Mar 31−Apr 2, 1996; Szejtli, J., Szente, L., Eds.; Kluwer: Dordrecht, The Netherlands, 1996; p 541.
(18) Soldatov, D. V.; Ripmeester, J. A. *Chem. Mater.* **2000**, *12*, 1827.
(19) Estevao, L. R. M.; Nascimento, R. S. V. *MRS Symp. Proc.* **1999**, *576*, 287.
(20) Estevao, L. R. M.; Nascimento, R. S. V. *Corros. Sci.* **2001**, *43*, 1133.

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