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CURIOUS ASSOCIATIVE/DYNAMIC PROPERTIES OF PERFLUOROCARBON MODIFIED VINYL POLYMERS IN SOLUTIONS, BLENDS AND IN THE SOLID STATE

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Perfluorocarbon (RF) groups attached as pendent groups to aqueous polymers (polyacrylamide and similar polymers) via spacer groups of various lengths have shown extraordinary hydrophobicity compared with hydrocarbon groups of similar lengths as shown by NMR, and rheology studies. Large RF mediated increases in polymer association especially for longer spacer groups were observed for a wide range of these polymers. In addition, blends of well-defined C_4F_9 , C_7F_{15} , $C_{10}F_{21}$ and $C_{13}F_{27}$ end-functionalized polystyrene (RF-PS) and poly(n-butylmethacrylate) prepared by ATRP using RF-tagged initiators. Blends of these polymers have been studied by DSC, AFM, TEM and optical transmittance. The AFM micrographs show crater, necklace and other RF mediated morphologies indicating the presence of submicron RF micelles that mediate

blending. More recently RF-PS polystyrenes end-functionalized with longer perfluoroalkyl ($RF=C_7F_{15}$, $C_{10}F_{21}$, $C_{13}F_{27}$) groups were studied using DSC, nano-indentation and other properties. These showed pronounced increases in storage and especially loss moduli compared with polystyrene polymers having the same molecular weights hence indicating an important role especially of the $C_{13}F_{27}$ groups in both increasing both storage and mechanical loss moduli. The RF groups appear to be present as micelles. Interestingly, compared with the matching PS, the glass transition temperatures of the $C_{13}F_{27}$ -PS polymers were found to decrease by as much as 15°C being seen for longer RF groups consistent with rapid dynamics in the $C_{13}F_{27}$ micelles below 100°C.

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