hydrophobic ligands further into the solvent. For this system the dependence of rate constants and mixture properties on composition shows a rapid decrease in g_k when alcohol is added to the aqueous solution containing the iron(II) complex and hydroxide ions. In terms of the initial state (= complex + OH^-), we anticipate that preferential hydration of OH^- by water is the dominant influence leading to $G_{1\neq} \simeq 0$ with $G_{1is} > 0$, and hence $g_k < 0$, becoming more negative with increase in x_2. In terms of the transition state we anticipate that the hydrophobic interactions with added alcohol results in $G_{2\neq} > 0$ and hence $g_k < 0$. By incorporating the activation volume data, we see that $|g_{k1}| > |g_{k2}|$ which we associate with the preferential solvation of OH^- in the mixture by water. These trends continue until around $x_2 = 0.2$. In fact, Figure 4 highlights the way in which the structure of the binary solvent mixture and the properties of solutes in the mixture are closely linked. The properties of the mixture lead to a subdivision in terms of mole fraction ranges. At low mole fraction x_2 the added alcohol enhances water–water interactions. As more alcohol is added, water–water cooperative hydrogen bonding attempts to maintain local water-rich domains with incipient tendencies to partial miscibility. As still more alcohol is added, the system takes on the character of a mixture of a polar and a nonpolar liquid in which the alcohol disrupts water–water hydrogen bonding. The situation is akin to that indicated by the thermodynamic properties when liquid CCl_4 is added to liquid methanol. Indeed as revealed by the Kirkwood–Buff integral functions in Figures 3 and 4, in a liquid mixture where $x_2 > 0.3$, there is little preferential solvation, the composition of the cospheres being not very different from that of the bulk mixture.

In both examples discussed above, the structural models that emerge from the Kirkwood–Buff integral functions offer an interesting insight into solvent effects on kinetics of reactions in binary aqueous mixtures and the basis of a quantitative approach for probing the role of preferential solvation in kinetics. This type of approach is clearly superior to analyses of medium effects which require that rate constants are plotted as a function of parameters measuring macrosopic solvent properties. We contend that kinetic medium effects treated by using SWAG[4] or, as here, Kirkwood–Buff models offer possibilities for quantitative insights into the interactions that govern the solvent effects on rate constants and offer possibilities for using medium effects as effective probes for mechanistic studies in physical organic chemistry.

Acknowledgment. We thank Professor Y. Yoga and Professor M. Sakurai for sending us complete sets of data and preprints of papers concerning enthalpies and volumes of mixing respectively of 2-methyl-2-propanol + water mixtures. We thank SERC for a grant to H.J.C., the University of Leicester for a travel grant to M.J.B., and the Hickinbotham Charitable Trust for their support.

Small PbS Clusters Prepared via ROMP Block Copolymer Technology

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Received March 5, 1990

Abstract: Small particles of lead sulfide have been prepared by H_2S treatment of block copolymer films wherein aggregates of poly[$(C_7H_9CH_2C_5H_4)_2Pb$] reside as microdomains distributed throughout a polynorbornene matrix. The block copolymers were prepared by sequential addition of 200 equiv of norbornene and 5, 10, and 20 equiv of $(C_7H_9CH_2C_5H_4)_2Pb$ (**1**) to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2), followed by quenching with benzaldehyde. The interdomain spacings (320–480 Å) before and after H_2S treatment were revealed by small-angle X-ray scattering (SAXS). Average cluster diameters (20–40 Å) were determined by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). The clusters were identified as PbS by X-ray fluorescence analysis performed on the STEM and by wide-angle X-ray powder diffraction.

In the past 5 years, several groups have shown that the electronic structure of a semiconductor varies with particle size[1] and that semiconductor clusters with diameters in the range 20–100 Å exhibit nonlinear optical properties.[2] In order to exploit the potential of these materials fully, it is necessary that the clusters be as close to a single size as possible.[1b] Workers have achieved varying degrees of success at controlling cluster growth in zeolites,[3] borosilicate glass,[4] colloids,[5] hydrophobic/hydrophilic random copolymers,[1c,d] and reverse micelles,[6] among other methods.[7] In this paper, we disclose a new approach that takes advantage of microdomain formation,[8] a phenomenon that has been shown to result in spherical, cylindrical, or sheet morphologies, most notably for polystyrene/polybutadiene block copolymers.[9] We employ Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2),[10] an especially mild ROMP (ring-opening metathesis polymerization) catalyst[11] that is relatively tolerant of functionalities.

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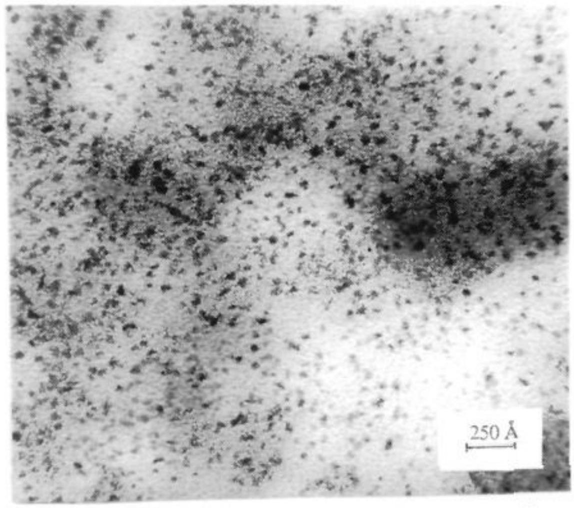
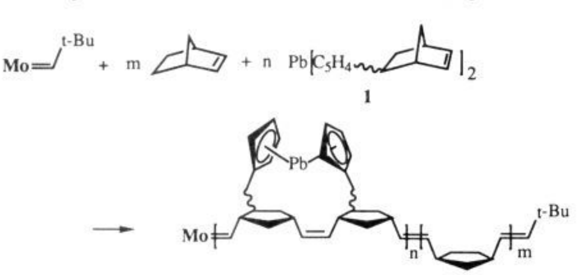


Figure 1. Bright-field STEM micrograph of **3b**. (The grainy background is observed for polynorbornene homopolymer.)

Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ does not react with an excess of PbCp$_2$ (Cp = η^5-C$_5$H$_5$) in C$_6$D$_6$. Under *ideal* circumstances, the sequential addition of norbornene and **1** (eq 1) to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ should yield the block copolymer shown in eq 1.[12] Three living block copolymers (m_{av} = 200; n_{av} = 5, 10, 20; eq 1) were prepared in toluene at 25 °C. The chains were cleaved from the metal in a Wittig-like reaction using benzaldehyde, and ~0.5 mm films (n_{av} = 5 (**2a**), 10 (**2b**), 20 (**2c**)) were then cast directly from the reaction mixtures by slow evaporation of solvent. These transparent films retained the yellow color inherent to **1**. Analysis of the three films (**2a–c**) by small-angle X-ray scattering (SAXS) showed a microphase-separated morphology in which the average distances between the Pb-containing domains were 320 (±50) Å (**2a**), 420 (±50) Å (**2b**), and 480 (±50) Å (**2c**).



(1)

When the three films were treated with H$_2$S (1 atm), their color changed from yellow to orange to red in less than 2 h. (PbCp$_2$ reacts instantaneously with H$_2$S in organic solvents to give black PbS.) They were left under H$_2$S for a total of 12 h in order to ensure complete conversion of all organic lead to PbS (eq 2). It

$$\mathbf{2a\text{–}c} + \mathrm{H_2S}\ (1\ \mathrm{atm}) \rightarrow (\mathrm{PbS})_x \text{ in block copolymer} \quad (2)$$

$$\begin{array}{l} \mathbf{3a}\ (n_{av} = 5) \\ \mathbf{3b}\ (n_{av} = 10) \\ \mathbf{3c}\ (n_{av} = 20) \end{array}$$

was shown by SAXS that the Pb-containing regions in films, **3a–c** were separated by 330 (±50) Å (**3a**), 480 (±50) Å (**3b**), and 400 (±50) Å (**3c**). Scanning transmission electron microscopy (STEM) confirmed that what are believed to be PbS clusters in essentially a polynorbornene matrix are irregular but roughly spherical in shape with a size distribution of 10–30 Å (**3a**), 20–50 Å (**3b**), and 25–50 Å (**3c**) (Figure 1). Although the trend is toward larger clusters with increasing *n*, the fairly large distribution in cluster size in each sample prevents definitive confirmation of the trend. The spacing between Pb-containing regions determined by STEM confirms that determined by SAXS.

The particles were identified as PbS by a combination of X-ray fluorescence analysis and wide-angle X-ray diffraction. An X-ray density map of Pb and S (with the overlapping Pb Mα signal at 5.28 Å and S Kα signal at 5.37 Å[13]) for sample **3b** correlates with the corresponding dark-field STEM image, and the atom % ratio of Pb and S was found to be 1:1. X-ray powder diffraction patterns showed peaks characteristic of PbS (at 2θ = 26°, 30°, 43°, 51°),[14] in addition to a strong peak at 2θ = 18.5° due to polynorbornene.[15] The PbS peaks were approximately 4 times more intense in **3c** than in **3a**.

Preliminary visible spectra suggest that the absorption edges for samples **3a–c** shift to longer wavelengths as *n* increases (from ca. 600 to 750 nm). Confirmation must await synthesis and examination of relatively thin samples prepared by spin coating.

The results presented here suggest that a ROMP block copolymer approach to semiconductor cluster synthesis is feasible. Future studies will involve a monomer that has only one polymerizable double bond and nonexchangeable Pb. We expect to be able to prepare essentially monodisperse block copolymers containing Pb-rich domains in which the distribution about the mean number of leads is much smaller than is evidently the case here.[16] We are also extending this technique to the synthesis of other semiconductors such as CdS and CdSe.

Acknowledgment. We thank the National Science Foundation (Grant DMR 87-19217) and Nippon-Zeon for financial support and A. J. Garrett-Reed and M. Frongillo of the MIT Electron Microscopy Facility for valuable assistance.

Supplementary Material Available: Detailed description of experimental procedures (2 pages). Ordering information is given on any current masthead page.

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