$$K_{eq} = \frac{k_1}{k_2} = \frac{[GV]}{[GH][V]} \quad (1)$$

$$R = \frac{d[NAD^+]}{dt} = \frac{k_{cat}}{K_m}[G][LDH] \quad (2)$$

$$[G] = \frac{[GH](k_d + k_3K_{eq}[V])}{k_h + k_4[V] + \frac{k_{cat}}{K_m}[LDH]} \quad (3)$$

$$\frac{1}{R} = \frac{1}{[LDH]}\left[\frac{k_h + k_4[V]}{[GH]\frac{k_{cat}}{K_m}(k_d + k_3K_{eq}[V])}\right] + \frac{1}{[GH](k_d + k_3K_{eq}[V])} \quad (4)$$

It is assumed that [GH] is essentially equal to the total glyoxylate concentration since $k_h/k_d > 100$,[7,8] and it is expected, by analogy with the case of esterification by vanadate of the hydroxyl group of lactate,[4] that $K_{eq}[V] < 0.01$. The concentrations of monomeric vanadate, [V], were calculated from the vanadium atom concentrations and the equilibrium constants for formation of vanadate oligomers, as described elsewhere.[9] Initial estimates for the parameters of eq 4 were obtained from appropriate plots of the data shown in Figure 1, and then a nonlinear least-squares program (BMDP) was used to fit eq 4 to all of the data shown in Figure 1. The values thus obtained were as follows: $k_d = 0.0098 \pm 0.0002$ s^{-1}, $k_3K_{eq} = 12.7 \pm 0.8$ M^{-1}·s^{-1}, $k_h/(k_{cat}/K_m) = 0.034 \pm 0.009$ mg·mL^{-1}, $k_4/(k_{cat}/K_m) = 36 \pm 28$ mg·mL^{-1}·M^{-1}. Similar values were obtained when the experiment was repeated by using lower concentrations of [LDH], and the values were not affected by changing the concentration of glyoxylate.

The value obtained for k_d is similar to that obtained by other investigators under similar conditions with the same experimental method.[7] From the value of k_3K_{eq}, an estimate can be made for k_3 if it is assumed that the value of K_{eq} is similar to the corresponding value obtained for lactate. The value of K_{eq} for lactate, 0.5 M^{-1}, was obtained at 1.0 M ionic strength, pH 7.35, but it is a reasonable first approximation to use for K_{eq} in Scheme I. By using a value of 1.0 M^{-1} for K_{eq}, to take into account the presence of two hydroxyl groups on GH, $k_3 = 12.7$ s^{-1}. This value is more than 10^2 times that reported for the elimination of phosphate from the phosphorylated hydrate of glyceraldehyde at 15°, pH 7.5 This difference could be due to the negatively charged carboxylate group on glyoxylate or possibly to the ease with which the V–O bonds can undergo rehydridization upon elimination of vanadate. It is also possible that the reactive species GV is a complex in which GH acts as a bidentate ligand in the same way that lactate can.[4] Similar cyclic complexes have been proposed to rationalize catalysis of other dehydration reactions by transition metals.[10,11]

By using the published value of 163 for k_h/k_d at 25°, pH 7.4[8] as an approximation for k_h/k_d under the conditions used here, and the value determined above for k_d, the value of k_h can be estimated at 1.60 s^{-1}, and $k_4 = k_3k_{eq}k_h/k_d = 2.1 \times 10^3$ M^{-1}·s^{-1}.

We conclude that vanadate is an electrophilic catalyst of aldehyde dehydration and a nucleophilic catalyst of aldehyde hydration. Since there is evidence that oxalyl thioesters, formed from glyoxylate, act as intracellular messengers for insulin and some other hormones,[8,12] it is reasonable to consider whether the type of chemistry reported here might be responsible for some of the physiological effects of vanadium.[13,14]

Acknowledgment. This work was supported by a grant from the Medical Research Council, Canada.

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Chemical Potential Driven Contraction and Relaxation by Ionic Strength Modulation of an Inverse Temperature Transition

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The sequential polypentapeptide of elastin,[1,2] (L-Val^1-L-Pro^2-Gly^3-L-Val^4-Gly^5)$_n$, when cross-linked by γ-irradiation and when in equilibrium with water undergoes a reversible contraction on raising the temperature from 20 °C to 40 °C.[3] That this is the result of an inverse temperature transition has been shown by many physical characterizations[4] and is also evidenced by observing in water that analogues which are more hydrophobic undergo the transition at lower temperatures,[5] whereas less hydrophobic analogues undergo the transition at higher temperatures.[6] In this communication, it is demonstrated that a change in salt concentration causes a shift in the temperature of the inverse temperature transition and in particular that contraction and relaxation can be achieved by such changes in ionic strength. To our knowledge, this is the first demonstration that changes in chemical potential can produce contraction and relaxation in a neutral polymer and in particular in a synthetic polypeptide containing only aliphatic (Val and Pro) or no (Gly) side chains where the process is one of ionic strength modulation of an inverse temperature transition.

The polypentapeptide was synthesized as previously described.[7,8] This material is soluble in water in all proportions below 25 °C but on raising the temperature aggregation occurs.[9] Aggregation may be monitored by following the temperature dependence of solution turbidity as shown in Figure 1A for water and for phosphate buffered saline (0.15 N NaCl, 0.01 M phosphate) which is the physiological buffer system. In Figure 1A it is seen that phosphate buffered saline (PBS) causes aggregation to begin at a lower temperature while the effect of pH, curves a and b Figure 1A, is minimal, almost within the reproducibility of the data. The aggregates settle to form a more dense phase called the coacervate which in water is 38% peptide and 62% water by weight at 40 °C.[9] The coacervate is a viscoelastic phase which can be formed

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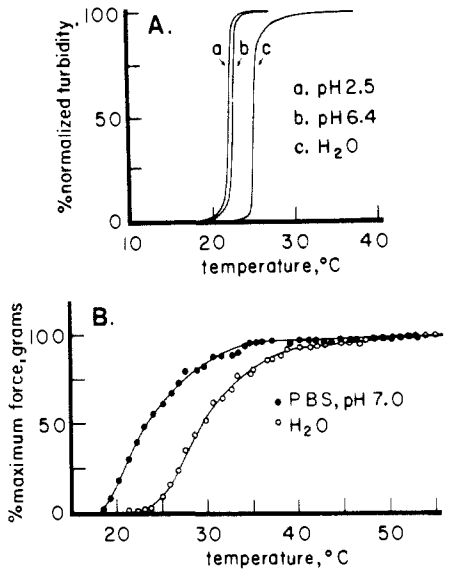

Figure 1. A. Temperature profiles for turbidity formation (aggregation) for 40 mg polypentapeptide/mL as the temperature is scanned from low to high temperatures at a rate of 30 °C/h. In phosphate buffered saline (PBS) the curves were determined at low (2.5) and near neutral (6.4) pH values to demonstrate the minimal effect of pH on the temperature of the transition. B. Thermoelasticity curves for an elastomeric band of cross-linked polypentapeptide. The sample in water of dimensions 0.76 × 4.06 × 5.44 mm^3 at 37 °C and zero load was stretched to 40% extension at 37 °C, and at this fixed length of 7.62 mm the temperature was lowered to below 20 °C for overnight equilibration, and then the temperature was raised at a rate of 1 °C per hour while monitoring force. The medium was then changed to PBS (pH 7); the sample was equilibrated at low temperature, and again the force was monitored as the temperature was raised. The forces at 37 °C were 3.2 g for water and 2.88 g for the subsequent PBS run.

in any desired shape and then γ-irradiation cross-linked at 20 Mrad (20 × 10^6 radiation absorbed dose) to form an elastomeric matrix.[7] Within the limits of nuclear magnetic resonance detectability for carbon-13 and nitrogen-15 enriched polypentapeptide, the coacervate is essentially indistinguishable from the cross-linked elastomeric matrix[10,11] demonstrating that γ-irradiation results in no NMR detectable breakdown of the polypentapeptide. Elastomeric bands so prepared can be characterized by stress/strain and thermoelasticity studies in a previously described apparatus.[12] When the sample is equilibrated in solution at 37 °C and stretched to 40% extension and the force is monitored as a function of temperature at the fixed extension, the thermoelasticity curves of Figure 1B are obtained for water and for PBS where elastomeric force is seen to develop abruptly at temperatures which approximately correspond with the temperature profiles of turbidity formation of Figure 1A. As the presence of PBS causes the development of elastomeric force to occur at lower temperature, it should be possible to remain at a fixed intermediate temperature, for example, at 25 °C, and to achieve contraction and relaxation by changing between water and PBS solutions. This is shown in Figure 2A for conditions of a fixed extension (28% extension at 25 °C in PBS) while monitoring force and in Figure 2B for conditions of a fixed force (1.6 grams obtained at 20% extension in PBS at 25 °C). Thus the polypentapeptide of elastin is seen to exhibit mechanochemical coupling in response to changes in ionic strength of the medium. Furthermore as seen in Figure 2, there is essentially complete reversibility of relaxation and contraction.

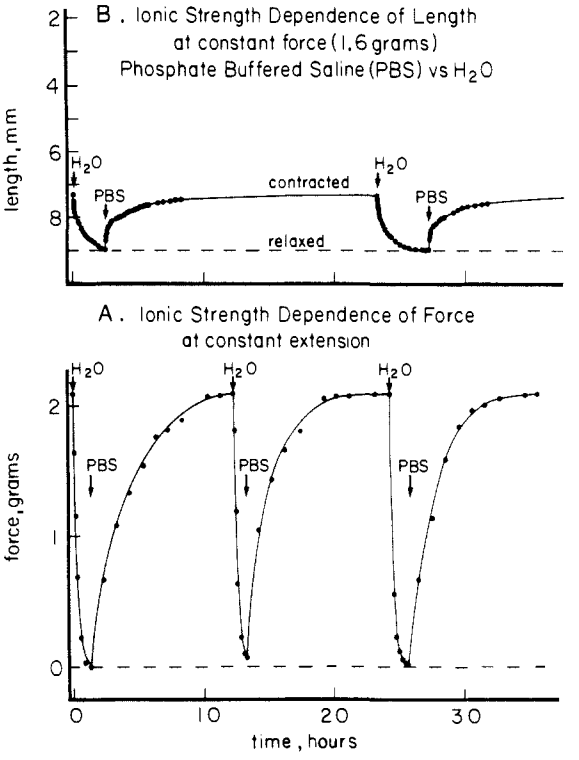

Figure 2. A. Force changes at constant extension due to changing the medium between PBS (pH 7) and water at 25 °C with reference to 28% extension above the zero load length in PBS at 25 °C. The sample dimensions at 25 °C in PBS at zero load were 0.7 × 3.56 × 5.72 mm^3. A slow irreversible swelling of the sample occurred during the time course of the experiment from an initial length of 5.72 mm to a final length of 6.06 mm as determined at zero load. B. Length changes at constant force (1.6 g obtained at 20% extension in PBS at 25 °C) due to changing the medium between PBS and water. The sample dimensions at 25 °C in PBS at zero load were 0.7 × 3.76 × 6.06 mm^3. This experiment immediately followed that of part A. The dry weight of the sample was approximately 5 mg; the sample can develop forces and pick up weights 1000 times its own weight.

That the transition is an inverse temperature transition with increase in order within the polypeptide part of the system on increasing temperature has been demonstrated by numerous physical characterizations.[4] For example, by light and electron microscopy the aggregation process has been seen to be a process of self-assembly into anisotropic fibers comprised of parallel aligned filaments;[4] by circular dichroism spectroscopy the polypeptide backbone is seen to go from a less-ordered to a more-ordered state on raising the temperature through the transition;[9] dielectric relaxation studies on increasing the temperature through the transition show the development of an intense localized relaxation near 10 MHz[13] indicating the development of the same motional process in each of the pentamers, and, by nuclear magnetic resonance relaxation studies on increasing the temperaure of the coacervate concentration, the backbone mobility decreases as the temperature is raised through the transition.[10,11] By nuclear magnetic resonance,[14] circular dichroism,[9] and Raman[15] spectroscopies and X-ray crystallography[16] of cyclo(VPGVG)$_3$ and poly(VPGVG), the conformation of the polypentapeptide has been shown to be that of a recurring Pro^2-Gly^3 Type II β-turn with a Val^1C-O···HNVal^4 hydrogen bond. Furthermore a slow thermal denaturation is seen above 60 °C.[4] A description of inverse temperature transitions in water began with the early general work of Frank and Evans[17] which was extended to proteins by Kauz-

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mann[18] and to biological membranes by Tanford[19] and which has more recently been treated in general by Ben Naim[20]. The understanding of the inverse temperature transition is that more-ordered clathrate-like water surrounding the hydrophobic side chains below the transition becomes less-ordered bulk water above the transition as intramolecular and intermolecular contacts involving hydrophobic side chains occur. The decrease in length, which is from the contraction due to the inverse temperature transition at zero load and 40 °C, is to 45% of the 20 °C length,[3] i.e., the length changes by greater than a factor of 2.[21]

Studies on collagen by Katchalsky and colleagues[22,23] are particularly relevant to the present report. Collagen fibers undergo a melting or denaturation of structure with shrinkage in length on raising the temperature, and increasing certain salt concentrations such as LiBr, KSCN, and urea[22] lowers the temperature of the transition. Attending the melting is a contraction to almost one-half of the native length. By using these properties, Katchalsky and co-workers[23] devised a mechanochemical engine which could be driven by a pair of baths, one containing 11.25 M LiBr and the other containing water or dilute (0.3 M) LiBr. This followed work on the contraction of polyelectrolyte (polymethacrylate) fibers where decreased charge–charge repulsion was the mechanism of contraction[24-27] with 50% ionization being required to get the extended state. In the present demonstration, mechanochemical coupling is achieved with a polypeptide containing no charges, and it is the temperature of an inverse temperature transition rather than a regular transition that is being shifted by the charge in chemical potential of the salt solution.

Experimentally modulation of an inverse temperature transition is achievable with smaller changes in chemical potential (less chemical work) which is consistent with the small endothermic heat of the inverse temperature transition, i.e., the heat of polypentapeptide coacervation is about 2 cal/gram (unpublished data). Accordingly, this provides a particularly favorable type of system for free-energy transduction. In principle, of course, desalination could be achieved by driving such a polypentapeptide-based mechanochemical engine backwards. Since the more favored ionic interaction with the polypentapeptide would be cationic interaction with carbonyl oxygens and since this would lead to charge accumulation on the polypeptide with the consequence of charge–charge repulsion, increased cation interaction with polypeptide on raising salt concentration would not seem to be the mechanism with which to bring about contraction. As demonstrated, by carbon-13 NMR spectra, neither does the presence of salt alter the very small amount of Val-Pro cis peptide bond. If the effect of increasing NaCl concentration is not to bind polypeptide as a means of favoring the contracted state of the polymer, then it would seem necessary to consider the effect of increasing ionic strength on the structure of the clathrate-like water which would be to lower the temperature of the transition by destabilizing the clathrate-like water structure of the low-temperature relaxed state.[28]

Acknowledgment. This work was supported in part by National Institutes of Health Grant HL 29578 and the Department of Navy, Office of Naval Research contract N00014-86-K-0402. We also acknowledge the technical assistance of Bryant Haynes and John Jaggard.

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Synthesis of Boron Carbide via Poly(vinylpentaborane) Precursors

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Received December 22, 1987

Limitations in traditional ceramic processing have encouraged interest in the development and utilization of polymer pyrolyses as low-temperature synthetic routes to nonoxide ceramic materials.[1,2] Boron carbide is an example of a material where preparation from a polymer precursor might offer advantages[2] over conventional synthetic techniques.[3] Mixed B_4C–SiC ceramics have, in fact, been previously obtained from pyrolysis of poly(carboranesiloxane)[4] polymers; however, a synthesis of pure B_4C from polymeric precursors has heretofore not been developed. We report here that 2-$(H_2C{=}CH)$—B_5H_8 will undergo thermal polymerization to vinylpentaborane oligomers and that these species can be converted to pure boron carbide (B_4C) in high ceramic yields under mild conditions.

In a recent paper,[5] we showed that the complex $[Cp^*IrCl_2]_2$, in the presence of Proton Sponge, catalyzed reactions of pentaborane(9) with acetylenes resulting in the high yield formation of alkenylpentaboranes. Vinyl polymers derived from these compounds would be particularly attractive precursors to boron carbide since they appear to obey several of the criteria previously identified by Wynne and Rice[1] for successful ceramic synthesis from polymers. First, pentaborane(9) has a low decomposition temperature, thus imparting low thermal stability to a polymer and enabling the material to decompose at moderate temperatures. Second, polymer structures containing rings or cages, such as pentaborane(9), should readily undergo a solid-state cross-linking step which is necessary to ensure that molecular fragments are not liberated during pyrolysis.

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