Preliminary studies towards crosslinking polymerizations with tetraethynylmethane and its derivatives: evidence for unusually facile alkyne hydration

Ken S. Feldman,*[a] David A. Mareska,[a] Carolyn K. Weinreb[a] and Manish Chasmawala[b]

[a] *Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA*
[b] *Department of Polymer Science, The Pennsylvania State University, University Park, PA 16802, USA*

Tetraethynylmethane and its derivatives are oligomerized to afford inhomogeneous, intractable solids which have undergone significant *in situ* alkyne hydration

Carbon network preparation *via* alkyne coupling has recently received a great deal of attention as the physical properties of such assemblies might be of interest in several areas of materials science.[1–3] Syntheses of linear[4–7] and planar macrocyclic[8–12] model polyalkynyl oligomers have been achieved, although to our knowledge no subsequent polymerizations to afford characterized materials have been reported. Glaser coupling-type polymerizations of polyalkynylated planar monomers (*e.g.* polyacetylenic aromatics) to yield highly crosslinked but inhomogeneous carbon rich materials have been described.[13] The architectures of these solids are a matter of speculation, but the possibility that these planar monomers might afford three-dimensionally crosslinked networks remains remote.

Tetraethynylmethane **1** (TEM), which has been synthesized in 100 mg quantities,[14,15] has been postulated as a building block for such a three-dimensional construction.[3] The feasibility of manipulating TEM and its derived monomers **2**–**4**[15] to yield highly crosslinked polymers was probed with one of two transition metal-mediated acetylene coupling procedures.

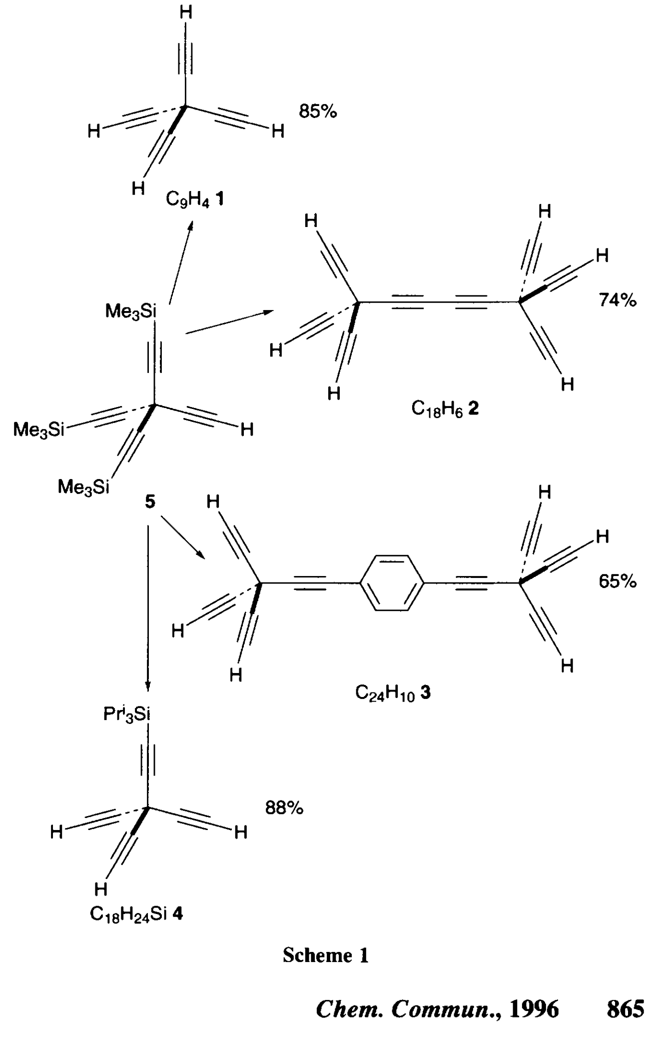
The direct coupling of acetylenes **1**, **2** and **4** was achieved with the use of copper (I) in acetone under an oxygen atmosphere at room temperature (Table 1).[16] In each case, an insoluble black solid precipitated over a period of approximately 20 h. Caution was warranted in this general procedure as the isolated solids occasionally proved to be explosive, perhaps as a consequence of inadequately extracted copper impurities.† These solids were successively washed with water, methanol and ethyl acetate, followed by continuous Soxhlet extraction with acetone for 24 h. Solvent and any remaining moisture was removed by drying the resulting solids at 100 °C/1.0 mm Hg for another 24 h over P_2O_5. Expansion of this putative three-dimensional architecture with a phenyl 'spacer' was explored as well. Thus, combination of TEM monomer **3** with 1,4-diiodobenzene *via* palladium (0)[17] catalysis afforded an insoluble brown solid. This material was collected, washed and dried as described above.

Table 1 Polymers resulting from sp–sp and sp–sp^2 coupling protocols

Entry	Monomer	Conditions[a]	ρ[b]/ g cm^{-3}	Ideal elemental analysis	Actual elemental analysis[c]
a	**1**	i	1.6	C	$C_9H_{5.4}O_{4.7}$
b	**2**	i	1.5	C	$C_9H_{5.0}O_{3.6}$
c	**4**	i	1.2	$C_{18}H_{21}Si$	$C_{18}H_{23.6}Si_{0.9}O_{6.7}$
d	**3**	ii	1.6	$C_{21}H_8$	$C_{21}H_{11}I_{0.9}O_3$
e	**3**	ii	1.7	$C_{21}H_8$	$C_{21}H_{10}I_{1.3}O_{2.5}$
f	**3**	iii	1.5	$C_{21}H_8$	$C_{21}H_{13.7}I_{0.4}O_{3.4}$
g	**3**	iii	1.4	$C_{21}H_8$	$C_{21}H_{12.1}I_{0.3}O_{3.2}$

[a] i, CuCl, O_2, TMEDA; ii, $PdCl_2$, CuI, PPh_3, HMTP, IC_6H_4I; iii, $Pd(PPh_3)_4$, CuI, MeONa, IC_6H_4I. [b] Approximated *via* flotation in organic liquids.[18] [c] Cu: 0.2–4%/entry: Pd: < 1% entry g.

The insolubility of the solids produced by these procedures has hindered attempts to completely characterize them, although the data obtained address the type of functionality present and the qualitative extent of crosslinking. Elemental analysis, FT-IR and CPMAS ^{13}C NMR (for entry d) all point to incomplete coupling and further chemical modification of the derived alkyne connections. Terminal alkyne absorptions in the IR spectra of all of these reaction products, and significant iodine content in the arylated entries, are clear indications of interrupted polymerization. In the Cu-mediated reactions (entries a–c), oxidative coupling leads to the curious and counterintuitive observation that H:C actually increases relative to the monomeric precursors. A similar increase in hydrogen content accompanies the non-oxidative Pd-mediated couplings as well (entries d–g). An explanation for these



Scheme 1

unexpected results can be gleaned from the IR and ^{13}C NMR spectra of these solids. Clear ketonic carbonyl adsorptions are detected in each entry: 1700–1725 cm^{-1} in the materials produced by Cu-mediated coupling, and 1680 cm^{-1} in the Pd-derived arylated solids. In addition, a broad signal at δ 195 in the ^{13}C NMR spectrum of the material produced in entry d is consistent with the presence of aryl ketones. Taken together, these data point to substantial alkyne hydration as the source of both the high H : C ratio and the unexpected oxygen content in these oligomerization products. Similar alkyne hydration does not accompany formation of simple TEM dimers (*e.g.* the silylated precursors to **2** or **3**) under identical experimental conditions. Thus, it is plausible that incorporation of the alkynes into a partially formed network introduces an added element of strain which facilitates hydration under mild conditions.

The thermal stability of the polymers and their behaviour at elevated temperatures were also examined. Polymer products of copper and palladium couplings from monomers **3** and **4** were studied *via* thermal gravimetric analysis under an argon atmosphere with heating at 10 °C min^{-1}. Each polymer experienced onset of weight loss at approximately 300 °C which continued steadily as the temperature increased to 800 °C (instrument limit). Typical overall weight loss is nearly 50% and the degradation is so uniform and severe that it makes examination of these systems *via* differential scanning calorimetry impossible. The gases released upon heating the solid from polymerizing **3** and **4** were analysed by GC-MS electron impact ionization over 25–550 °C. Major fragments corresponding to hydrogen iodide, iodobenzene and diiodobenzene were identified from the palladium-coupled polymer.

Perhaps the difficulty of forming the desired hypercross-linked polymers *via* these metal-mediated protocols lies in the drastic change in bond geometry that must accompany conversion of the organometallic intermediates into the final carbon–carbon coupled products. The alkynes and/or alkynyl–aryl precursors are likely to bond to the transition metal in a *cis*-fashion (*e.g.* an approximately 90° bond angle) prior to reductive elimination. However, upon C–C bond formation, this angle expands to the linear 180° found in the products. The energetic barrier associated with this change may be insurmountable.

We thank the National Science Foundation (NSF CHE 93-21787) for financial support.

Footnote

† Explosions were observed with monomer **2**, the polymer derived from **2** (entry b) and the polymeric material resulting from Glaser coupling of ethyl 3,3-bisethynylpent-4-ynoate (not shown). The latter solid detonated upon grinding either in air or under an argon atmosphere. The solid formed from **2** exploded upon either grinding or heating to 100 °C. The monomer **2** exploded while being impregnated on SiO_2 (room temp.). These substances did not explode every time they were manipulated, and the basis for sensitivity with one batch and not another is unclear at present.

References

1 U. H. F. Bunz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1073.
2 F. Diederich, *Nature*, 1994, **369**, 199.
3 (a) F. Diederich and Y. Rubin, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1101; (b) J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler and F. Diederich, *Helv. Chim. Acta*, 1995, **78**, 13.
4 R. Eastmont, T. R. Johnson and D. R. M. Walton, *Tetrahedron*, 1972, **28**, 4601.
5 R. Eastmont and D. R. M. Walton, *Tetrahedron*, 1972, **28**, 4591.
6 T. R. Johnson and D. R. M. Walton, *Tetrahedron*, 1972, **28**, 5221.
7 R. J. Lagow, J. J. Kampa, H. C. Wei, S. L. Battle, J. W. Genge, D. A. Laude, C. J. Harper, R. Bau, R. C. Stevens, J. F. Haw and E. Munson, *Science*, 1995, **267**, 362.
8 A. M. Boldi and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 468.
9 L. T. Scott, M. J. Cooney and D. Johnels, *J. Am. Chem. Soc.*, 1990, **112**, 4054.
10 Q. Zhou and P. J. Carroll, *J. Org. Chem.*, 1994, **59**, 1294.
11 L. T. Scott, G. J. DeCicco, J. L. Hyun and G. Reinhardt, *J. Am. Chem. Soc.*, 1985, **107**, 6546.
12 A. De Meijere, S. Kozhushkov, C. Puls, T. Haumann, R. Boese, M. J. Cooney and L. T. Scott, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 869.
13 T. X. Neenan, M. R. Callstrom, L. M. Scarmoutzos, K. R. Stewart and G. M. Whitesides, *Macromolecules*, 1988, **21**, 3525.
14 K. S. Feldman, C. M. Kraebel and M. Parvez, *J. Am. Chem. Soc.*, 1993, **115**, 3846.
15 K. S. Feldman, C. K. Weinreb, W. J. Youngs and J. D. Bradshaw, *J. Am. Chem. Soc.*, 1994, **116**, 9019.
16 A. S. Hay, *J. Org. Chem.*, 1962, **27**, 3320.
17 K. Sonogashira, Y. Tohda and H. Hagihara, *Tetrahedron Lett.*, 1975, 4467.
18 *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, Florida, USA, 72 edn., 1991.

Received, 30th November 1995; Com. 5/07821K