Use of Unmodified Carbohydrate Reagents for the Polymerization of Dicyanoalkenes and Dicyanoarenes[§]

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In this communication, we describe the polymerization of several dicyanoalkenes and -arenes to high molecular weight conjugated polymers using initiation by *unmodified* carbohydrate reagents under mild conditions. The polymers either have not been previously prepared or, in one case, have improved thermal properties compared to closely related polymers prepared by other routes.

Several polymerizations using *modified* carbohydrate reagents for initiation have been described. Bicyclic *N*-acetyl-D-glucosamines have been used[1] to initiate living polymerization of 2-oxazolines. Ethyl glucopyranoside has been described[2] as a multifunctional initiator for enzyme-catalyzed lactone and carbonate polymerization. Protected sugar-based tertiary bromides have been used[3,4] as initiators in atom transfer radical polymerization. Protected carbohydrates have been used to introduce chirality into polymers in cyclopolymerization experiments.[5]

We have recently reported[6] that 2-benzylidene-4, 5-dicyano-1, 3-dithiole (**1**) (see Scheme 1 for structures)-undergoes cyclopolymerization with lithium butoxide in 1-butanol and other reagents to give a semiconducting fluorescent conjugated material with a weight-average molecular weight in the range 14 000−60 000. This polymerization is unusual because all previous reactions of dicyanoalkenes and -arenes with alkoxides in alcohols led to cyclotetramerization, the best-known example being the phthalocyanines.[7−11] In the interest of testing mechanistic hypotheses that avoid the well-known[7−11] cyclotetramerization, we are studying weak reducing agents, such as sugars.

We initially found that **1** reacted with sucrose in methanol in the presence of alkali to give a polymer similar to that from butoxide in 1-butanol in 55% yield (Table 1). This polymer had a visible spectrum very similar to that reported,[6] and its ^{1}H and ^{13}C NMR spectra were similar to those previously[6] obtained with weak resonances in both, suggesting the presence of covalently bound sugar-derived moieties. Using gel permeation chromatographic (GPC) analysis in *N,N*-dimethylformamide (DMF) solution containing 0.5 wt % LiBr vs polystyrene standards, we found (Table 1) $M_w = 19\,300$ and $M_w/M_n = 1.10$. In the absence of LiBr, the apparent molecular weights exceed 200 000, suggesting aggregation. This observation is also made for several of the other systems discussed below. Thermogravimetric analysis (TGA) revealed onset of weight loss at 208 °C, compared to 160 °C for the polymer from butoxide in 1-butanol.[6] A similar polymer was obtained in 75% crude yield from **1**, lactose, and NaOH in methanol. With an electronic spectrum very similar to that obtained from **1** and sucrose, this polymer exhibited $M_w = 13\,600$ and $M_w/M_n = 1.89$ (Table 1). The structure deduced for these polymers is given in Scheme 2.

Table 1

monomer	carbohydrate	% yield, purified polymer	M_w (M_w/M_n)	TGA onset of weight loss (°C)
1	sucrose	55	19 300 (1.10)	208
1	lactose	40	13 600 (1.89)	168
2a	glucose	26	11 900 (1.75)	120
3	glucose	59	12 200 (1.20)	175
3	methylglucopyranoside	77	9 200 (1.18)	170
2c	glucose	98	40 200 (1.76)	115
2d	glucose	50	7 200 (1.38)	115
4	glucose	64	56 000 (1.55)	115

Reaction of 4-nitrophthalonitrile (**2a**) with glucose and NaOH in methanol also results in cyclopolymerization to a black material that retains small quantities of DMF in 26% yield. This polymer from **2a** exhibits a broad intense electronic absorption spectral maximum at 703 nm. While metal-free cyclotetramers of phthalonitrile (**2b**) and its derivatives exhibit[7−11] intense absorption maxima near 700 nm with vibrational subbands approximately 35 nm in width,[11] the spectrum of the polymer from **2a** is different in appearance and markedly broader than that of cyclotetramers, tailing to 1000 nm. The M_w for this polymer is 11 900 and $M_w/M_n = 1.75$.

While **1** and **2a** react with sugars and alkali in a cyclopolymerization process, only one cyano group reacts in reactions of alkaline glucose in methanol with 4-amino- (**2c**) and 4-(dimethylamino)phthalonitrile (**2d**), tricyanovinyldimethylaniline[12] (**3**, TCVDMA), and 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine[13] (**4**). The evidence for reaction at one cyano group follows from observation of cyano infrared absorption near 2200 cm^{-1} and the ^{13}C NMR resonance for a cyano group at a chemical shift of about 115 ppm in each of these polymers, as we have reported[14,15] for products from **2b,e.** The infrared and ^{13}C NMR spectra of the polymer from **4** are exhibited in Figure 1. The yields, molecular weights, and temperatures for the onset of weight loss (TGA) of the polymers from these monomers are given in Table 1. Since the polymers from **2c** and **4** are not sufficiently soluble to obtain ^{13}C spectra in solution, these spectra were obtained using cross-polarization and magic angle spinning (CPMAS) techniques. Structure **5** is assigned to the polymer from TCVDMA on the basis of its visible spectrum with a maximum at 429 nm, similar to 4-(dimethylamino)benzylidenemalononitrile.[16] The polymer from TCVDMA exhibits a fluorescence maximum at 502 nm on excitation at 399 nm. Some hydrolysis of cyano groups in **2a**, for example, is indicated by IR absorption near 1730 cm^{-1} and ^{13}C resonance near 170 ppm. This is also indicated in reactions of **2b** and 4-methoxyphthalonitrile (**2e**).[14,15]

The difference in the kind of polymer structure obtained from **1** and **2a** and **2c,d**, **3**, and **4** clearly merits discussion. For the cases of **2c,d**, resonance structures

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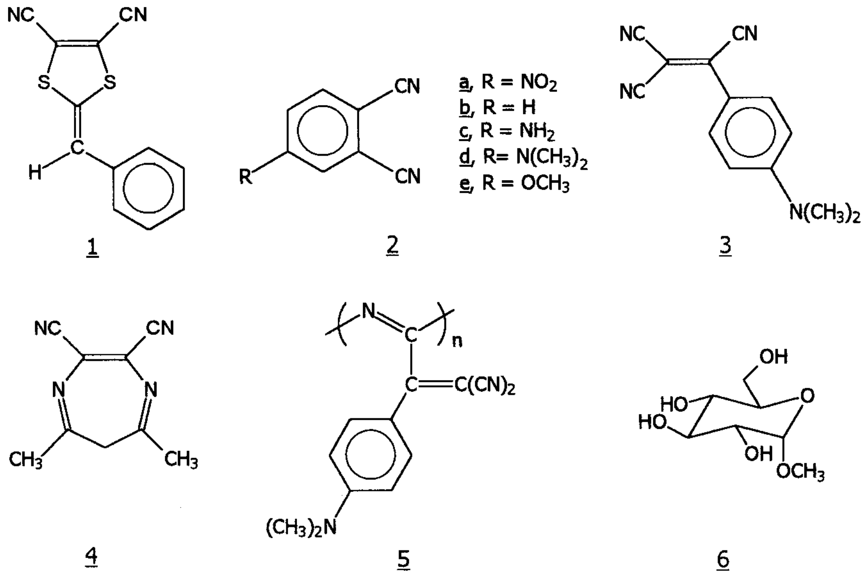
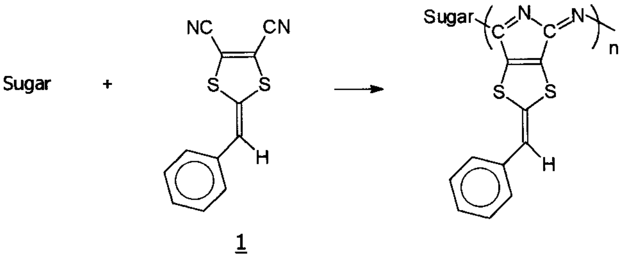
Scheme 1



Scheme 2



(see Supporting Information) suggest that the electron-releasing effect of R_2N would enhance electron density at the $-$CN group para to the R_2N group. Even if initial nucleophilic addition occurred at the $-$CN group meta to the R_2N group, an anion on the substituent meta to the R_2N group would encounter the excess electron density at the cyano group para to R_2N. In contrast to the electron-releasing amino groups in **2c,d**, the 1,3-dithiole ring in **1** and the nitro group in **2a** would tend to decrease electron density at the cyano groups in their molecular structures, possibly facilitating cycloaddition leading to cyclopolymerization.

It is also relevant to identify the site on a sugar responsible for initiating polymerization. In Figure 1, the relatively weak ^{13}C resonances between 60 and 100 ppm are consistent[17] with attachment of the sugar at the hemiacetal carbon. For TCVDMA, reaction with methylglucopyranoside (**6**) and alkali (Table 1) leads to the same polymer (77% yield) as obtained from glucose. Since the anomeric 1-carbon associated with the reducing properties of sugars is blocked in **6**, reaction is then initiated by an alkoxide. This might also be applicable to polymerization of **1** with sucrose, not a reducing sugar. The 2-OH position on sucrose is the most reactive in nucleophilic additions.[18] These experiments contrast sharply with others reported[14,15] in reactions of **2b** with sugars and alkali. In those experiments, mixtures of cyclotetramer (yields up to 25%) and an oligomer revealing reaction at one cyano group (yields up to 55%) are obtained. When these reactions are attempted with species that lack the hemiacetal reducing function, namely **6**, gluconolactone, ascorbic acid, D-sorbitol, and inositol, neither of the above products is formed.

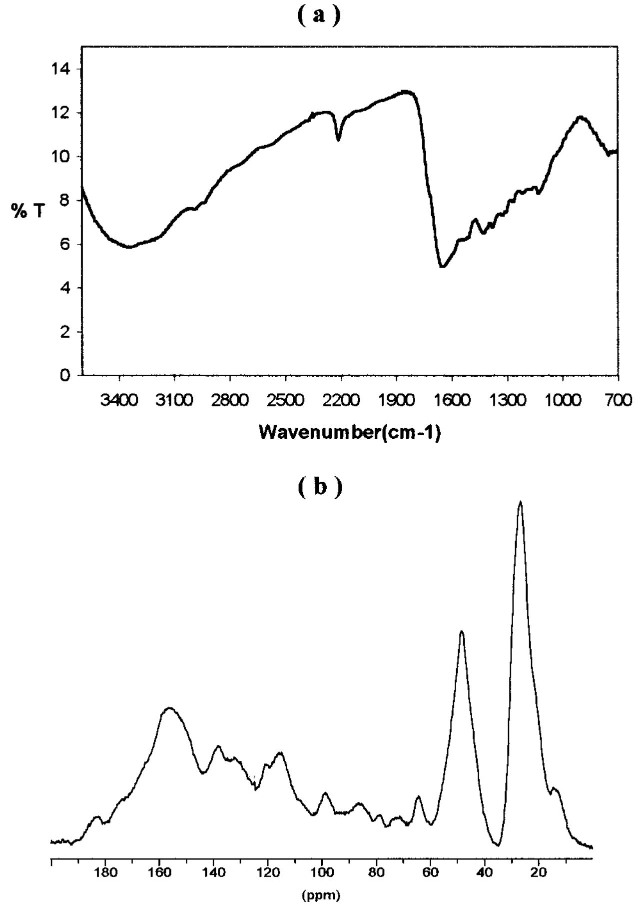


Figure 1. (a) Fourier transform infrared spectrum of the polymer from **4** and glucose. Note cyano absorption near 2200 cm^{-1}. (b) ^{13}C CPMAS NMR spectrum of the polymer from **4** and glucose. The resonances near 114 and 120 ppm are assigned to $-$CN, that at 155 ppm is assigned to C$=$N, and those at 64 and 99 ppm are assigned to the primary alcohol and anomeric carbon of a glucopyranose ring, respectively. The resonance near 185 ppm is a spinning side band.

In summary, we have observed for the first time polymerization reactions initiated by unmodified carbohydrate reagents. Our studies of further synthetic aspects, mechanistic issues, and materials properties continue.

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Supporting Information Available: Infrared and ^1H and ^{13}C nuclear magnetic resonance spectral data, differential scanning calorimetry and thermogravimetric analysis data, and elemental analysis data for new materials is given, along with a scheme showing resonance structures for **2c,d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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