

Functionalizable Self-Assembling Polydiacetylenes and Their Optical Properties

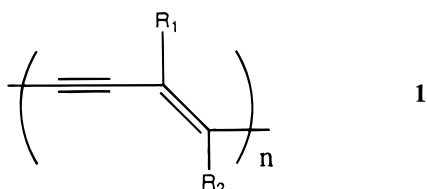
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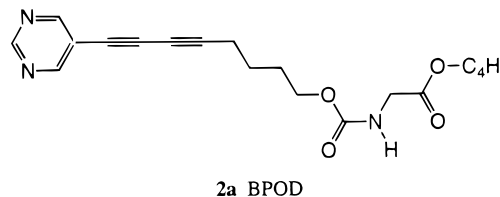
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Over at least the past decade, there has been considerable interest in the introduction of specific side groups into polydiacetylenes (PDA, **1**) to control properties such



as polymer chemical reactivity,¹ electronic structure,^{1,2} and spectroscopy,³ second-order nonlinear optical (NLO) properties,⁴ and chromic phenomena.⁵ In recent reports from our laboratories,⁶ the synthesis, acentric self-

assembly, and second-order NLO properties of the PDA of the *n*-butoxycarbonylmethylurethane (BCMU) of 1-(5-pyrimidyl)-1,3-octadiyn-8-ol (BPOD, **2a**) point to



a design paradigm that merits elaboration. In particular, we note three design features: (1) a conjugated backbone; (2) one side group as a chromophore; (3) the other side group with both aliphatic and hydrogen-bonded urethane groups to promote solubility and processability. The polymer was found to spontaneously self-assemble into an acentric order with significant second-order optical nonlinearity. We now report the synthesis of the alkoxycarbonyl-methyl urethanes of 9-(*N*-methyl-*N*-phenylamino)-5,7-nonadiyn-1-ol (**2b,c**) and their polymerization. We find that the polymers are soluble and processable and that the benzenoid ring group is susceptible to many of the substitution reactions expected for aromatic amines making it a more versatile system for chemical modification than the previously investigated systems.¹ We further describe novel self-assembling and linear and nonlinear optical properties of the modified polymers. These polymers, in addition to possessing the unusual assembly properties of PDA–BPOD, present some unique processing features. The azobenzene-functionalized PDA from **2b**, for example, was photofabricated to produce regular surface relief gratings. We conclude that the PDA from **2b,c** and their functionalized forms comprise the most versatile PDA system reported to date, in terms of chemical richness and diverse optical properties.

The synthesis of **2b,c** is illustrated in Scheme 1. Cadiot–Chodkiewicz coupling of *N*-methyl-*N*-propargylaniline and 5-bromohexyn-1-ol leads to 9-(*N*-methyl-*N*-phenylamino)-5,7-nonadiyn-1-ol (**2d**) in 74% yield. Reaction of this diacetylene alcohol with the appropriate isocyanate leads to **2b,c**; the yield of **2b** is 73%.

2b,c are viscous yellow oils at ambient temperature and did not polymerize in that phase on exposure to ultraviolet light. Crystallization was achieved as they were frozen in dry ice in evacuated ampules and polymerized in the solid state by exposure to 46 Mrad ⁶⁰Co γ radiation at a dose rate of 0.5 Mrad/h. The PDA from **2b,c**, obtained in approximately 40% yield after monomer removal, are red-colored solids that are found to be soluble in a manner similar to PDA–BPOD and –BCMU in solvents such as chloroform and *N,N*-dimethylformamide (DMF) with an absorption maximum at 473 nm (CHCl₃). The ¹³C NMR and Raman^{2a,b} spectra of the PDA from **2b,c** verify the assignment of the usual enyne backbone structure, and gel permeation chromatography of a chloroform solution of the PDA of **2b** reveals (relative to polystyrene) M_w 190 000, M_n 81 000, $M_w/M_n = 2.3$. PDA–BPOD spontaneously self-assembles into a noncentrosymmetric structure when

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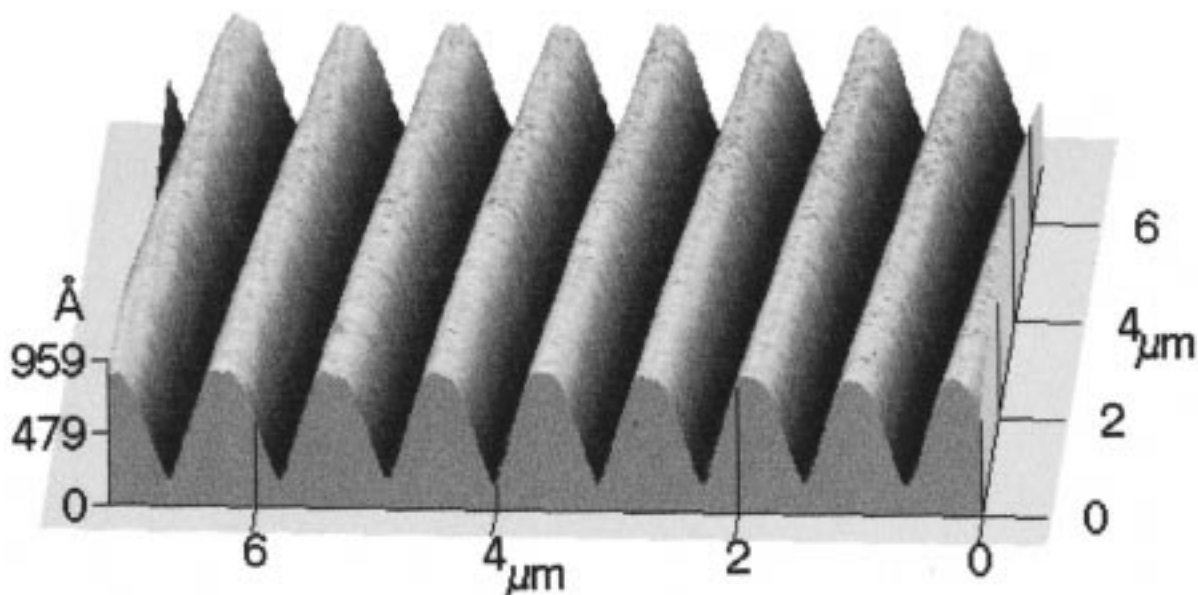
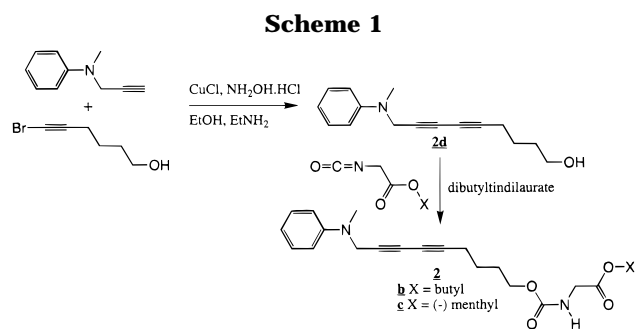
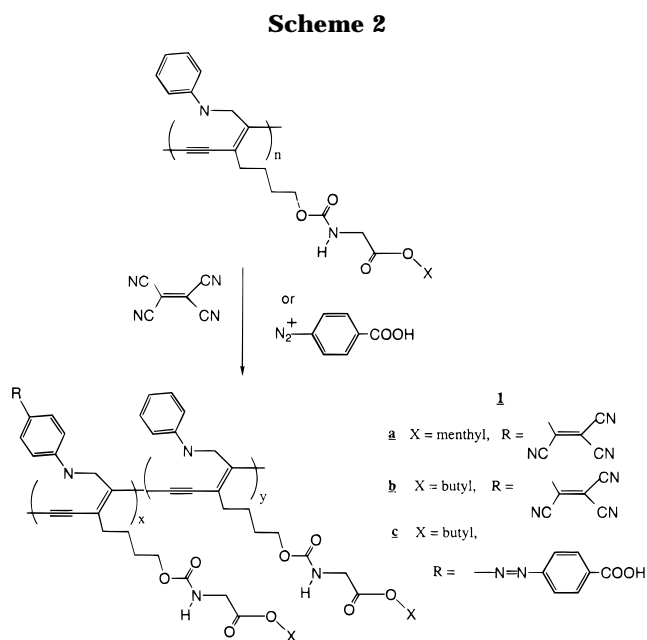


Figure 1. AFM image of a directly fabricated surface relief grating of PDA-1c. The image was recorded using an argon ion laser at 488 nm and a recording beam intensity of 50 mW/cm². The incident angle of the recording beams was 14°.



solution spin cast on various substrates. It was found that the PDA of **2b** also assembles into a noncentrosymmetric film from a frequency doubling experiment that gave a d_{33} value of 0.3 pm/V at 1.064 μm .

We have found that the aromatic ring of PDA of **2b,c** readily undergoes aromatic amine substitution reactions such as diazonium salt coupling and tricyanovinilation.⁷ These reactions have also been used to synthesize chromophores with significant values of the second-order nonlinear optical coefficient, and these reactions have been extended to polymers.⁸ In the present work, poly-**2c** reacts with excess tetracyanoethylene (TCNE) in DMF to give a PDA **1a** in quantitative yield with 40–45% of the aromatic rings tricyanovinylated (Scheme 2). This PDA is red in color with a broad visible



absorption maximum at 499 nm (CHCl₃) and soluble in chloroform and DMF. This postpolymerization functionalization of the anilino-functional PDA is a versatile route to the design of novel PDA. The solubility of the tricyanovinylated PDA is noteworthy in view of the following. Reaction of **2b,c** with TCNE in DMF leads to tricyanovinylated monomers **2e,f**. Solid-state polymerization of **2e,f** with ⁶⁰Co γ radiation (50 Mrad) leads to a 52% conversion of monomer to PDA, but, after monomer extraction, the PDA are insoluble in all solvents attempted to date.

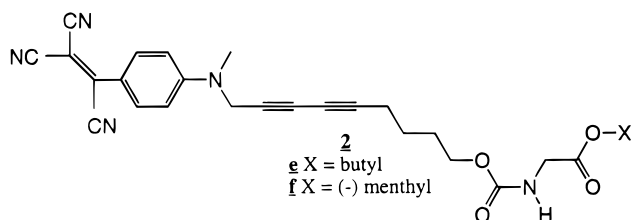
The presence of the tricyanovinylaniline chromophore in PDA **1a,b** invites assessment of second-order nonlinear optical properties.^{8,9} Spin-coated films of **1a** give a d_{33} value of 1 pm/V at 1.064 μm again without poling. The nature of the acentric order appears to be similar

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to that of a poled nonlinear optical polymer film. This was observed for the PDA–BPOD films as well.^{6a} It appears that the design paradigm of an acentric spontaneously self-assembled polymer can be extended at least to a number of asymmetrically substituted polydiacetylenes. The d_{33} coefficient increases to 33 pm/V after electric field poling at 130 °C for 30 min. The poling temperature was arbitrarily selected to be 130 °C given the fact that no thermal transitions were observed for this polymer until degradation around 200 °C. The d_{33} value is stable indefinitely at room temperature. The polydiacetylene backbone is assumed to be rigid with a large persistence length. The side groups, however, are expected to be sufficiently mobile at this temperature. The hydrogen-bonded network of the BCMU side groups for example is significantly disrupted at this temperature.¹⁰



The PDA from **2b,c** were also further functionalized by a postpolymerization azo coupling reaction.¹¹ In this process, the PDA of **2b** was reacted with the diazonium salt of *p*-aminobenzoic acid in *N,N*-dimethylformamide (DMF) to give a quantitative yield of PDA–**1c** (Scheme 2). The polymer was found by ¹H NMR to have 60% of the aromatic rings functionalized. No glass transition temperature (T_g) was observed from the DSC measurement of this polymer. Holographic surface relief gratings have been fabricated on azobenzene polymers.¹² The efficient trans–cis photoisomerization and relatively rapid reversal of the process make amino-substituted azobenzene materials attractive substrates to study the surface relief grating formation.¹³ Expo-

sure of a spin-coated film of an azobenzene polymer to an interference pattern from two polarized argon-ion laser beams at 488 nm leads to formation of such a grating.¹² An unusual characteristic of this fabrication process is that macromolecules are transported over significant distances while the sample is held substantially below its glass transition temperature, T_g . In the present study, we have fabricated surface relief gratings on azobenzene-functionalized PDAs for the first time. As shown in Figure 1, a typical surface relief grating in **1c** shows very regularly spaced sinusoidal surface structure with depth modulation of over 500 Å. The grating spacing can be adjusted by changing the angle between the two writing beams. These gratings have indefinite stability at room temperature. This provides the first example of such one-step photoinduced grating formation without postprocessing in a rigid-rod polymer (lacking a discernible glass transition). Such gratings are not formed with **1a,b** and the PDA from **2b**.

In summary, we have demonstrated a new case of side-group manipulation of PDA properties in a versatile self-assembling system. In particular, postpolymerization functionalization is a viable new strategy for the preparation of a whole range of new PDA materials that differs from the traditional approach of monomer synthesis followed by solid-state polymerization. In addition to the reactions described above, the PDA from **2b,c** react with other electrophilic reagents. Hence, as will be amply demonstrated in future publications, numerous additional novel PDA are at our disposal. Moreover, we have found that the PDA obtained via our postpolymerization functionalization have novel optical properties. Note that the polymer used to form the grating shown in Figure 1 is the first example of such grating formation in a rigid rod material.

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