*Macromolecules* **1999,** *32,* 7361−7369

# New Processable, Functionalizable Polydiacetylenes

**Mongkol Sukwattanasinitt,† Dong-Chan Lee,† Myunghwan Kim,† Xiaogong Wang,† Lian Li,‡ Ke Yang,§ Jayant Kumar,§ Sukant K. Tripathy,† and Daniel J. Sandman*,†**

*Center for Advanced Materials, Departments of Chemistry and Physics and Applied Physics, University of Massachusetts—Lowell, Lowell, Massachusetts 01854-2881 and Molecular Technologies, Inc., Westford, Massachusetts 01886*

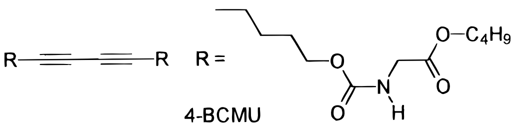
*Received May 18, 1999; Revised Manuscript Received August 19, 1999*

ABSTRACT: A new series of diacetylenes, 9-(arylamino)-5,7-nonadiynyl-*N*-(alkoxycarbonylmethyl)-urethanes was synthesized based on three design paradigms: (1) the polydiacetylene (PDA) conjugated backbone, (2) one side group as a chromophore, and (3) the remaining side group with components to promote solubility and processability. After exposure to $^{60}$Co $\gamma$-radiation, the resulting polydiacetylenes were highly soluble in many common organic solvents. These diacetylene monomers can be functionalized with ease not only before but after polymerization as well. Tricyanovinylation of diacetylene monomers followed by polymerization gave insoluble polymers, possibly due to strong interactions involving tricyanovinyl groups. However, tricyanovinylation after polymerization gave polymers soluble in common organic solvents with 45−55% degree of functionalization. The diazonium coupling reaction could also be carried out at the phenyl ring of the diacetylene monomer both before and after polymerization. In contrast to the intractable product from the direct polymerization of the azodiacetylene, postpolymerization diazonium coupling reaction yielded azobenzene-substituted polydiacetylene with good solubility in polar organic solvents. The degree of functionalization was in the same range as that of tricyanovinylated PDA. The second-order NLO coefficient ($d_{33}$) of the poled tricyanovinylated PDA (via postpolymerization functionalization) was found to be 33 pm/V at 1.136 $\mu$m. The photorefractive response of the tricyanovinylated PDA was demonstrated by two-beam-coupling measurements. The PDA-containing 4-[4-(carboxylic acid)phenylazo]aniline chromophores can directly be photomanipulated to form surface relief gratings.

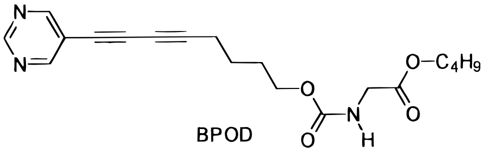
## Introduction

Polydiacetylenes (PDAs) are a class of conjugated polymers possessing potential photonic and electronic applications.[1] Photoconductivity, third-order optical nonlinearity, thermochromism, and solvatochromism are well-known interesting properties of PDAs. PDAs are typically obtained from topochemical polymerization of appropriate diacetylene (DA) monomers.

Substituents play important roles in creating crystal structures to control reactivities of the monomers as well as the properties of the corresponding PDAs. DAs having the same substituent at each end and containing flexible side chains, such as the urethane 4-BCMU[2a,b] or the ester ClCin22,[2c] are polymerized by UV light or $\gamma$-radiation, resulting in PDAs soluble in chloroform and other common organic solvents. Replacement of one of the urethane groups on a diacetylene such as 4-BCMU with a functional chromophore leads to numerous interesting possibilities. Recently, our center has reported studies on a novel asymmetric diacetylene, 1-(5-pyrimidyl)-1,3-octadiyn-8-ol (BPOD),[3] containing pyrimidyl and urethane groups.



4-BCMU



BPOD

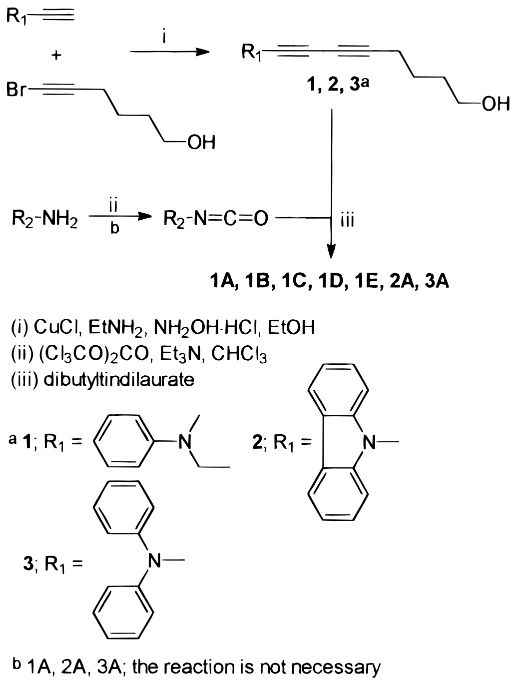
A high yield of soluble PDA was obtained by exposing this monomer to $^{60}$Co $\gamma$-irradiation. A spin-coated film of PDA−BPOD assembles into a noncentrosymmetric array as revealed by a significant second-order nonlinear optical (NLO) coefficient ($d_{\text{eff}} = 0.5$ pm/V at 1.54 $\mu$m).[4] However, corona poled films of PDA−BPOD did not show significant improvement of the *d*-coefficient. A few polymers obtained from other similar urethane-substituted DAs, containing nitrobenzene or azobenzene dyes, showed second-order NLO properties similar to PDA−BPOD, but most of them were insoluble in common organic solvents.[3d] Nevertheless, the attractive properties of PDA−BPOD suggest a design strategy that merits elaboration. Note three specific design features: (1) the PDA conjugated backbone; (2) one side group as a chromophore, preferably with the possibility of further chemical functionalization; and (3) the remaining side group has components to promote solubility and processability as in PDA−4-BCMU. In the present work, aliphatic and hydrogen-bonded urethane groups are used. Synthesis of such asymmetric DA can be quite tricky and tedious. It is thus of interest to find DAs that can be functionalized before or after polymerization as each DA in the latter case would provide numerous specifically functionalized PDAs. This paper presents synthesis, characterization, and some initial optical properties of a new series of DAs, 9-(arylamino)-5,7-nonadiynyl-*N*-(alkoxycarbonylmethyl)urethane. These new DAs contain a functionalizable arylamine group and various urethane chains. The presence of the arylamine group allows either pre- or postpolymerization functionalization. In a preliminary communication, the synthesis and polymerization of the (alkoxycarbonylmethyl)urethanes of 9-(*N*-methyl-N-phenylamino)-5,7-nonadiyn-1-ol were described along with initial information concerning second-order NLO properties

---

† Department of Chemistry.
‡ Molecular Technologies, Inc.
§ Department of Physics and Applied Physics.

10.1021/ma990776o CCC: $18.00

**Scheme 1. Synthetic Route for DA Monomers**



(i) CuCl, $EtNH_2$, $NH_2OH{\cdot}HCl$, EtOH
(ii) $(Cl_3CO)_2CO$, $Et_3N$, $CHCl_3$
(iii) dibutyltindilaurate

$^b$ 1A, 2A, 3A; the reaction is not necessary

and directly photofabricated surface relief gratings in the polymers.[5]

To demonstrate this advantage, tricyanovinylation was chosen due to its simplicity, and the resulting tricyanovinylarylamine chromophores possess a large hyperpolarizability.[6] To our knowledge, this is the first example of tricyanovinylation in a conjugated polymer system despite numerous examples reported in nonconjugated polymers.[7]

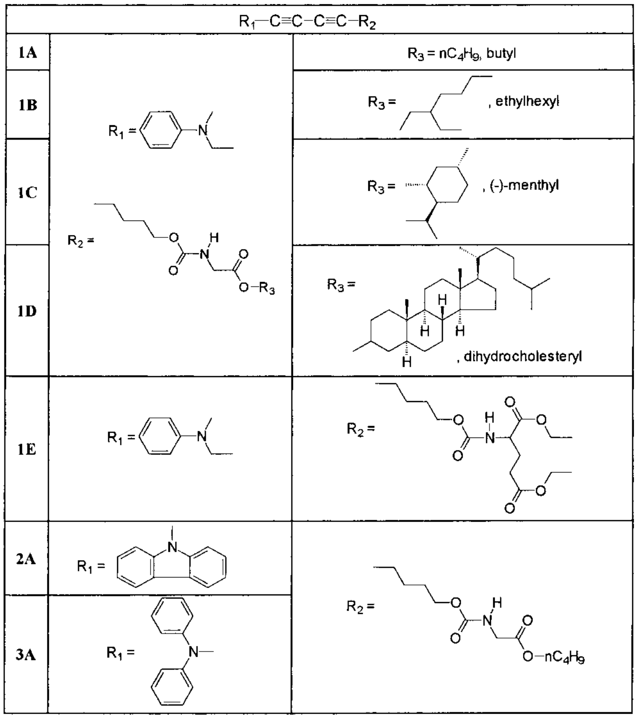
## Results and Discussion

The arylamine groups investigated in this work include *N*-methyl anilino, N-carbazolyl, and *N*,*N*-diphenylamino. Seven DAs (**1A**–**E**, **2A**, **3A**) were synthesized (Scheme 1 and Table 1) using ester substituted alkyl isocyanates,[8] 6-bromo-5-hexyn-1-ol,[9] *N*-methyl-*N*-propargylaniline,[10] *N*-propargylcarbazole,[11] and *N*-propargyldiphenylamine[12] as key starting reagents.

Cadiot–Chodkiewicz coupling[13] of *N*-methyl-*N*-propargylaniline, *N*-propagylcarbazole, and *N*-propargyldiphenylamine with 6-bromo-5-hexyn-1-ol afforded 9-(*N*-methyl-*N*-phenylamino)-5,7-nonadiyn-1-ol (**1**), 9-(*N*-carbazolyl)-5,7-nonadiyn-1-ol (**2**), and 9-(*N*,*N*-diphenylamino)-5,7-nonadiyn-1-ol (**3**), respectively, in 74%-86% yield. A reaction of this diacetylenic alcohol with an ester substituted alkylisocyanate, generated in situ from the corresponding alkylaminoester, yielded the desired urethane DA (**1A**–**E**, **2A**, **3A**) in 67–99% yields.[14] These diacetylenes were solids at room temperature except for **1A** and **1B**.

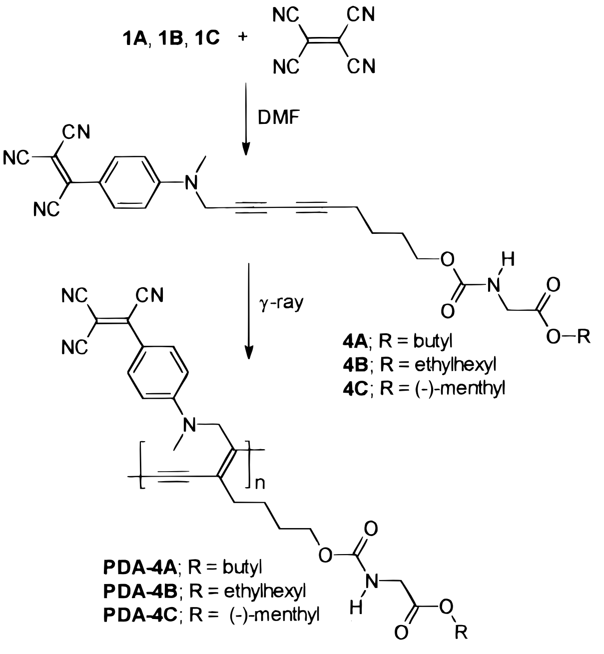
Tricyanovinylation of these DAs (**1A**–**C**) by the reaction with tetracyanoethylene (TCNE)[15] (Scheme 2) yielded the corresponding tricyanovinylated DAs (**4A**–**C**) as red solids.

**Table 1. Structure of DA Monomers**



| | $R_1$–C≡C–C≡C–$R_2$ | |
|---|---|---|
| 1A | $R_1$ =<br>$R_2$ = | $R_3$ = $nC_4H_9$, butyl |
| 1B | | $R_3$ = , ethylhexyl |
| 1C | | $R_3$ = , (-)-menthyl |
| 1D | O–$R_3$ | $R_3$ = , dihydrocholesteryl |
| 1E | $R_1$ = | $R_2$ = |
| 2A | $R_1$ = | $R_2$ = |
| 3A | $R_1$ = | O–$nC_4H_9$ |

**Scheme 2. Tricyanovinylation and Polymerization of DA Monomers**



**4A**; R = butyl
**4B**; R = ethylhexyl
**4C**; R = (-)-menthyl

**PDA-4A**; R = butyl
**PDA-4B**; R = ethylhexyl
**PDA-4C**; R = (-)-menthyl

These monomers were soluble in most common organic solvents. X-ray diffraction of a single crystal of **4B** gave the following lattice constants: $a = 4.94$ Å, $b = 29.36$ Å, $c = 87.21$ Å, $V = 12\,648.8$ Å$^3$, $Z = 16$, $\rho_{calc} = 1.167$ g/cm$^3$. Unfortunately, with only 600 reflections, it is not possible to solve the structure in a unit cell of this size. However, the fact that these monomers are highly sensitive to UV light and γ-radiation gives the certainty that these monomers have intermolecular dimensions that meet the requirement for solid-state polymerization. Polymerization of these tricyanovinylated DAs by exposing the monomers to $^{60}$Co γ-radiation (50 Mrad) resulted in insoluble dark red polymers (**PDA-4A**, **PDA-4B,** and **PDA-4C**). FT-Raman spectrum of **4C** contained C=C stretching (in the aromatic ring and the tricyanovinyl group) peaks at 1456, 1494, and 1538 cm$^{-1}$, a C≡N stretching peak at 2218 cm$^{-1}$, and a C≡C stretching peak at 2260 cm$^{-1}$. A weak C≡C stretching peak at 2122 cm$^{-1}$ from partially polymerized diacetylenes was also observed. The Raman spectrum of **PDA-4C** showed unresolved broad C=C stretching

**Scheme 3. Polymerization of DA Monomers**

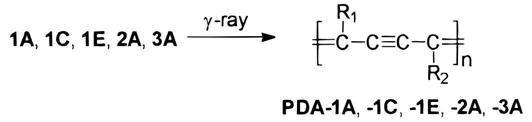


**Table 2. Purification Method and Polymerization Yield of PDAs**

| | purification method | polymerization yield (%) |
|---|---|---|
| **PDA-1A** | reprecipitation[a] | 39 |
| **PDA-1C** | reprecipitation[a] | 58 |
| **PDA-1E** | reprecipitation[a] | 63 |
| **PDA-2A** | Soxhlet extraction[b] | 35 |
| **PDA-3A** | Soxhlet extraction[c] | 57 |
| **PDA-4A** | Soxhlet extraction[c] | 52 |
| **PDA-4B** | Soxhlet extraction[c] | 100 |
| **PDA-4C** | Soxhlet extraction[c] | 58 |
| **PDA-6E** | Soxhlet extraction[c] | 20 |

[a] $CH_2Cl_2/CH_3OH$. [b] $CHCl_3$. [c] Acetone.

**Table 3. Absorption Maximum of PDAs[a]**

| | $\lambda_{max}$ (solution) (nm) | $\lambda_{max}$ (film) (nm) |
|---|---|---|
| **PDA-1A** | 473 | |
| **PDA-1A−TCV** | 499 | |
| **PDA-1C** | 469 | 470 |
| **PDA-1C−TCV** | 504 | 494 |
| **PDA-1E** | 465 | 479 |
| **PDA-2A[b]** | 440, 487 (sh[c]), 542 | 490, 544 |
| **PDA-3A** | 470 | 497 |
| **PDA-5A[d]** | 432 | |
| **PDA-6E[e]** | 450 | |

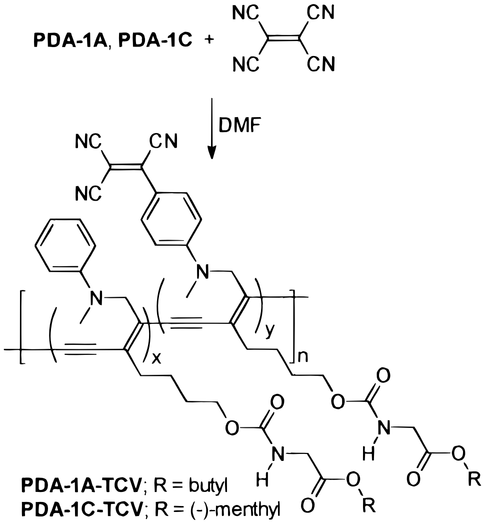
[a] Absorption maximum in solution was measured in $CHCl_3$ except for footnotes *b*, *d*, and *e*. [b] Absorption maximum in solution was measured in HMPA. [c] sh = shoulder. [d] Absorption maximum in solution was measured in DMF. [e] Absorption maximum in solution was measured in aqueous KOH (pH = 10).

**Table 4. Summary of Polymerizability and Solubility of DAs and PDAs**

| polym.[a] solids | unpolym. liquids | unpolym. solid | soluble polymers | insoluble polymers |
|---|---|---|---|---|
| 1A | | | **PDA-1A[b]** | |
| 1C | | | **PDA-1C[b]** | **PDA-4A** |
| 1E | 1A | | **PDA-1E[b]** | |
| 2A | | 1D | **PDA-2A[c]** | **PDA-4B** |
| 3A | | | **PDA-3A[b]** | |
| 4A | 1B | | **PDA-1A−TCV[b]** | **PDA-4C** |
| 4B | | | **PDA-1C−TCV[b]** | |
| 4C | | | **PDA-6E[d]** | |

[a] Polym. = polymerizable. [b] Solvents: DMF and $CHCl_3$. [c] Solvents: *N*,*N*-dimethylacetamide, HMPA. [d] Solvent: aqueous (pH > 10).

**Scheme 4. Postpolymerization Functionalization of PDA: Tricyanovinylation**



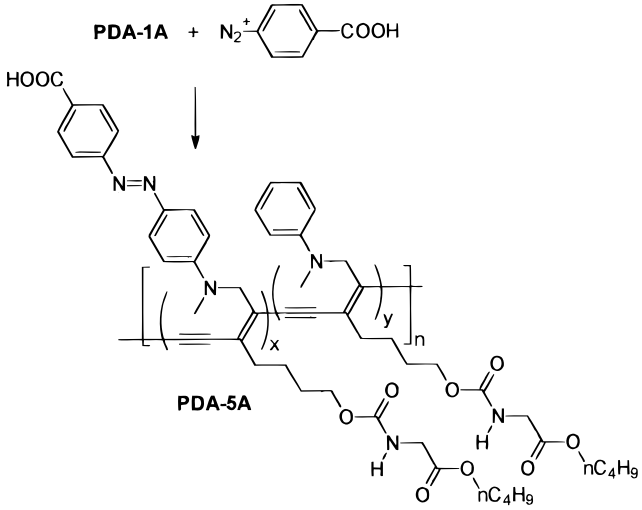
peaks centered at 1499 $cm^{-1}$ and a C≡C stretching of the typical PDA peak at 2106 $cm^{-1}$.[16] The insolubility of **PDA-4A**, **PDA-4B**, and **PDA-4C** may be due to strong intermolecular interactions involving tricyanovinyl groups. Auspiciously, polymerizable solid of **1A** was able to be obtained via crystallization of the monomer in ether−petroleum ether at −78 °C. Rapid evaporation of the solvents by a rotary evaporator, without warming the solution, gave a white solid when freshly prepared. The solid gradually turned red due to surface polymerization by the room light. **1A** melted at 15 °C, below room temperature. The polymerizable solid form of **1B** has not yet been obtained by the same crystallization procedure. **1D** was, on the other hand, an unreactive (to UV light, $\gamma$-rays, and heat) solid at room temperature. Polymerizations by $\gamma$-radiation were thus performed initially in a container packed with dry ice and **1A** or in an evacuated ampule with **1C**−**E**, **2A**, and **3A**. Soluble PDAs (**PDA-1A**, **PDA-1C**, **PDA-1E**, **PDA-2A**, and **PDA-3A**) were obtained in 30−60% yields from the exposure to 50 Mrad of $^{60}$Co $\gamma$-rays (Scheme 3 and Table 2).

The Raman spectrum of **PDA-1C** showed typical C=C and C≡C stretching of polydiacetylene at 1516 and 2108 $cm^{-1}$.[16] Electronic absorption spectra of **PDA-1A** in $CHCl_3$ showed a visible absorption band with a maximum at 473 nm, whereas **1A** did not absorb visible light. Other visible absorption maxima of soluble PDAs are summarized in Table 3.

$^{1}H$ NMR spectra of the polymers were similar to those of the monomers except for slight upfield shifts of aromatic and *N*-methyl proton signals and a broadening of the signals in the polymer spectra. $^{13}C$ NMR spectra of **PDA-1A** contained C≡C signals at 99.5 and 100.7 ppm and C=C signals at 128.5 and 131.4 ppm. Gel permeation chromatography (GPC) versus polystyrene showed bimodal chromatograms with number-average molecular weight of over 50 000 and polydispersity of 2.1−2.5. The reaction of these polymers with TCNE gave soluble partially tricyanovinylated polydiacetylenes (**PDA-1A−TCV** and **PDA-1C−TCV**) (see Table 4 for summaries of polymerizability of all the synthesized diacetylenes and solubility of all the synthesized polymers and Scheme 4 for the postpolymerization functionalization of PDA).

These partially tricyanovinylated polymers were obtained in virtually quantitative yields. FT-Raman spectrum of **PDA-1C−TCV** showing strong C=C and C≡C stretching peaks similar to those in **PDA-1C** indicated that the ene-yne remained intact in the polymer backbone. FT-IR spectrum of **PDA-1C−TCV** showed strong absorption due to C≡N stretching at 2216 $cm^{-1}$, implying an incorporation of tricyanovinyl groups to the polymer. The tricyanovinylation at the para position of the aniline groups was evidenced by visible absorption and $^{1}H$ NMR spectra. The electronic absorption spectra of **PDA-1A−TCV** in $CHCl_3$ showed a band with $\lambda_{max}$ around 500 nm (comparing to 473 nm of **PDA-1A**, Table 3) indicating the presence of typical 4-tricyanovinyl-*N*,*N*-dialkylaniline chromophores.[15] The $^{1}H$ NMR of **PDA-1C−TCV** showed a broad signal around 7.7−8.1 ppm corresponding to the aromatic proton ortho to the

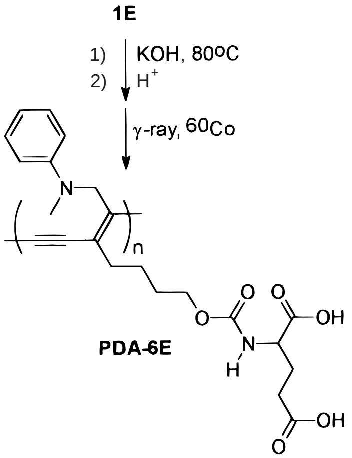
**Scheme 5. Postpolymerization Functionalization of PDA: Diazonium Coupling**



tricyanovinyl group. Integration of this $^1$H NMR from 7.7 to 8.1 ppm and from 6.9 to 7.2 ppm gave a degree of conversion of about 45% ($x = 0.55$ and $y = 0.45$), which agreed with elemental analyses. The accurate determination of the percent conversion for **PDA-1A–TCV** was hampered by an unremovable amount of solvent DMF. From several batches of this tricyanovinylation, the percent conversion was consistently within 45%-55%, even when the reaction was performed at elevated temperature (55 °C). Steric hindrance, which tricyanovinyl groups introduce to the side-groups of the PDA whose backbones are rather rigid, is probably a main cause of this limited conversion. Besides, the need to form a donor–acceptor complex as an intermediate in tricyanovinylation may limit the degree of conversion.[17] It is also reasonable to assume that the approximately 50% conversion corresponds to the alternating functionalization of the aromatic amine side groups. An azobenzene substituted polydiacetylene **PDA-5A** was obtained by postpolymerization diazonium coupling reaction (Scheme 5).[18]

The precursor polymer **PDA-1A** was reacted directly with the diazonium salts of *p*-aminobenzoic acid. FT-Raman spectrum of **PDA-5A** showed strong carbon–carbon double bond and triple bond stretching vibration. The similarity of the spectral character between **PDA-1A** and **PDA-5A** confirmed that the backbone ene-yne structure remain intact. The new peak corresponding to N═N stretch vibration at 1447 cm$^{-1}$ can be seen clearly from the Raman spectrum.[19] As shown from the UV–vis and $^1$H NMR spectra, the electrophilic substitution takes place exclusively at the 4-position on aniline moieties. The UV–vis spectrum of **PDA-5A** in DMF solution showed a strong absorption at 432 nm. The $^1$H NMR of **PDA-5A** showed a broad resonance around 8.00–7.60 ppm corresponding to the six protons ortho to the carboxylic acid and azo groups of the 4-[4-(carboxylic acid)phenyl-azo]aniline chromophores. By integration of this resonance and comparison with the resonance from the 6.5–6.8 ppm range of unreacted aniline moieties, a degree of functionalization of about 50% was obtained. The accurate determination of the percent conversion for **PDA-5A** suffers from the same problem as does **PDA-1A–TCV**. From different batches of this reaction, the percent conversion remains about the same.

**Scheme 6. Hydrolysis and Polymerization of DA**



Hydrolysis of **1E** followed by polymerization gave water soluble PDA (**PDA-6E**, Scheme 6) which furnished the fabrication of an ultrathin polymer film in aqueous medium by the programmed electrostatic layer-by-layer assembly technique. Electrostatic assembly was carried out by using PDA as polyanion and poly(diallydimethylammonium chloride) as polycation and gave a linear increase in the visible absorbance as the number of bilayers increases.[20]

## Properties

**Nonlinear Optical Properties.** Second-order NLO materials have shown considerable significance in photonic technology such as elecro-optic modulation, optical waveguide, and so on. Polymeric second-order NLO materials have a number of advantages over inorganic and organic crystals in terms of easy processability, flexibility and ease of design, synthesis, and fabrication. Moreover, due to a dielectric constant lower than that of its inorganic counterpart, high-speed electro-optic modulation can be achieved with second-order NLO polymers.[21] Among those second-order NLO polymers, donor–acceptor substituted PDAs could possibly be one of the best second-order NLO materials, which has been indicated by theoretical calculation.[22] Recently, synthesis and second-order NLO properties of asymmetrically substituted PDAs (PDA–BPOD) have been reported.[3b,4] These PDAs have spontaneously self-assembled into acentric arrays after spin coating without recourse to poling and showed significant second-order NLO properties.[4] Nonetheless, PDA–BPOD does not contain an effective second-order NLO active chromophore, i.e., donor–acceptor. It did not show any noticeable increase in second-order NLO properties with poling. The design paradigm of PDA in this report assesses second-order NLO properties by introducing appropriate chromophores, i.e., chromophores with hyperpolarizability.[6] A second-order NLO chromophore, the tricyanovinylaniline group, was introduced via postpolymerization functionalization to these asymmetrically substituted PDAs (Scheme 4). Spin-coated film of **PDA-1C–TCV** gave a $d_{33}$ value of 1 pm/V at 1.064 $\mu$m without poling, providing acentric spontaneous self-assembling of the second-order NLO chromophore. A higher degree of noncentrosymmetric alignment of the tricyanovinylaniline chromophores in **PDA-1C–TCV** was achieved by corona poling technique to increase the second-order NLO properties. No obvious glass-transition temperature was observed for this polymer by differential scanning calorimetry. The poling was thus performed at 130 °C for 30 min because higher mobility of the side groups is expected at higher temperatures. The second-order NLO coefficient ($d_{33}$), of the poled polymer film was measured at 1.136 $\mu$m by the second harmonic generation (SHG) technique. At this fundamental wavelength, the $d_{33}$ value was determined to be 33 pm/V. Again, it is noteworthy that this postpolymerization functionalization of the anilinofunctional PDA is a superior synthetic route to make soluble and processable PDAs with second-order NLO properties because direct polymerization of tricyanovinylanilino-functionalized diacetylenes (**4A**−**C**) gave insoluble polymers (**PDA-4A**, **PDA-4B**, and **PDA-4C**). The measurements of unpoled spin-coated films of **PDA-1A** and **PDA-1C** did not show significant SHG signals.

## Photorefractive Studies

Photorefractive materials are reported to have the possibility of exhibiting a large induced change in the index of refraction at modest light intensities.[23] These materials seem to be ideally suitable for real-time holographic applications because large nonlinear indices of refraction and fast response times are essential components for any optical data processing. Recently, photorefractive materials based on second-order NLO polymers have been investigated.[24] One of the approaches to prepare those materials is functionalizing polymers with all functional components, NLO-active moieties, charge generators, and charge-transporting agents.[25] Photorefractive materials based on conjugated polymers also have been studied[24b,26,27] and are expected to show faster photorefractive responses due to much larger carrier mobility than all other reported photorefractive polymers. In the present study, a second-order NLO active moiety, the tricyanovinylaniline-functionalized PDA (**PDA-1C**−**TCV**), was employed for the photorefractive studies. The preliminary studies using the two-beam-coupling (TBC) technique demonstrated that this polymer exhibits photorefraction. TBC phenomena (i.e., one of the interfering beams may gain energy while the other loses the same amount of energy) occurs when the change in intensity and refractive index patterns, induced by a light pattern, are phase-shifted. The TBC measurements with samples sandwiched between the patterned ITO slides and thin aluminum electrodes were carried out at a wavelength of 690 nm under an electric field of 400 kV/cm. The experimental result is shown in Figure 1. Clear asymmetric energy transfer between the two writing beams was observed.

## Regular Surface Relief Grating

In recent years, significant attention has been focused on surface relief gratings of azobenzene-containing polymers for holographic recording and other applications.[28] It is well-known that relatively fast and efficient trans−cis photoisomerization of the N=N bond under laser irradiation leads to surface relief grating formation. This behavior is due to large-scale polymer mass transport below its $T_g$.[29] The surface gratings on a conjugated polymer functionalized with azobenzene groups are expected to have synergism of potentially interesting optical and electronic properties. Surface relief gratings have been successfully photoinscribed on the azobenzene-functionalized PDA at room temperature.[5] Relief gratings with large depth modulation (>500 Å) have been accomplished. Figure 2 shows a typical atomic force microscopic (AFM) three-dimensional view of a grating formed on an azobenzene-functionalized PDA film (**PDA-5A**). It is clearly seen that the grating has a regularly spaced sinusoidal relief profile. It should also be pointed out that the photofabricated surface relief gratings are stable at room temperature. This provides an additional example of one-step photoinduced grating formation without postprocessing in a rigid-rod polymer. In conclusion, this is another particularly interesting example of the versatility of the postpolymerization functionalization approach.

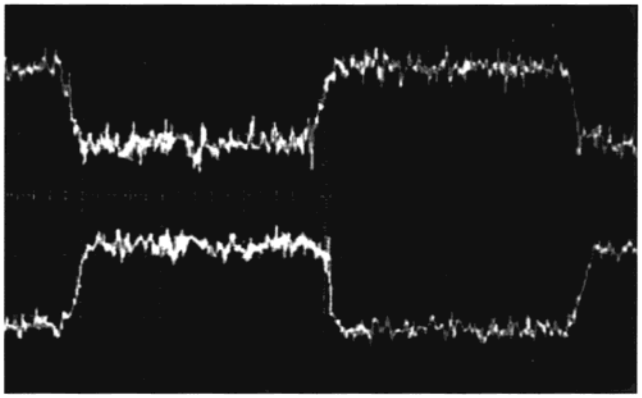


**Figure 1.** Asymmetric energy transfer of **PDA-1C**−**TCV** in the TBC experiment: one beam gains energy (top trace), another beam loses energy (bottom trace).

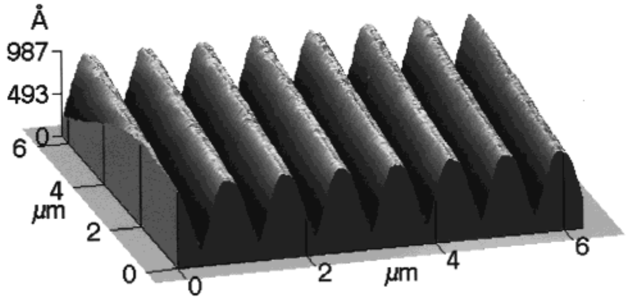


**Figure 2.** AFM image of a photofabricated surface relief grating of **PDA-5A**.

## Conclusion

Novel DAs with arylamino groups were synthesized. These DAs are functionalizable and polymerizable. The postpolymerization functionalization by tricyanovinylation and diazonium salt coupling showed an advantage in this system because the resulting polymers are soluble in common organic solvents. The poled polymers possess a relatively large second-order NLO coefficient, $d_{33}$. Photorefraction in tricyanovinylated PDA was observed. These anilinic DAs have proved to be among the most versatile monomers, allowing a number of other pre- and postpolymerization functionalizations. Surface relief gratings have been directly photofabricated on the azobenzene-functionalized PDA.

## Experimental Section

Characterization of synthesized compounds was based on elemental analysis, infrared, UV−vis, Raman, $^1$H NMR, and $^{13}$C NMR spectra. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. The IR spectra were recorded on a Perkin-Elmer 1720 FT-IR spectrometer from neat samples or samples dispersed in KBr pellets. The FT-Raman experiments were performed by exciting neat solid samples with a cw Nd:YAG laser at 1.064 $\mu$m, and the spectra were recorded on the same IR spectrometer with a Raman accessory in a 180° optical collection geometry. The UV−vis spectra were acquired on a Perkin-Elmer Lambda 9 spectrophotometer. The $^{1}$H and $^{13}$C NMR were collected on a Bruker ARX 200 MHz spectrometer from deuterochloroform solutions unless otherwise specified.

Ethylhexyl-, dihydrocholesteryl-, and menthylglycinate,[8] 6-bromo-5-hexyn-1-ol,[9] *N*-methyl-*N*-propargylaniline,[10] *N*-propargylcarbazole,[11] and *N*-propargyldiphenylamine[12] were prepared in our laboratory according to the literature. Tetracyanoethylene (TCNE) was sublimed prior to use. Other commercially available chemicals were used as received from vendors. *N*-Methylaniline, 2-ethylhexanol, (−)-menthol, (+)-dihydrocholesterol, L-glutamic acid diethylester hydrochloride, carbazole, and *N*,*N*-diphenylamine were purchased from Aldrich Chemical Co., butylisocyanatoacetate was purchased from Acros Organics, and 5-hexyn-1-ol was purchased from GFS.

**Nonlinear Optical Properties.** The second-order NLO coefficient ($d_{33}$) of the poled polymer sample was measured by SHG. The measurement was carried out with a laser radiation at a wavelength of 1.136 $\mu$m from an optical parametric oscillator pumped with a Q-switched Nd:YAG laser at 355 nm (Spectra-Physics). The SHG signal at 568 nm, selected with an IR-blocking colored glass filter and an interference filter, was detected by a photomultiplier tube and measured with a boxcar integrator (Stanford Research System). A Y-cut quartz crystal was used as the reference. By comparing the SHG intensity from the poled polymer sample with that from the quartz crystal, the *d* coefficient of the poled sample was determined. The refractive indices and thicknesses of the polymer film were measured with an ellipsometer (Rudolph Research) and a profilometer (Dektak IIA), respectively.

**Photorefractive Properties.** The TBC experiments were performed to investigate the photorefractive behavior of the polymeric material. A diode laser (LaserMax) and a digital oscilloscope (Hewlett-Packard) in conjunction with a mechanical chopper were used for the measurements. The measurements were carried out at room temperature with two p-polarized beams at a wavelength of 690 nm. An electric field of 400 kV/cm was applied across the sample.

**Surface Relief Gratings.** The surface relief gratings on the azofunctionalized PDA films were photofabricated. Two linearly polarized laser beams with an intensity of the order of 50 mW/cm$^2$ at 488 nm from an Ar$^+$ laser (Coherent) were utilized. The writing time of the relief gratings are about 30 min. The grating period could be varied by adjusting the angle between the two interfering laser beams. An AFM (Park Scientific) was employed for characterizing the surface relief structures of the photofabricated gratings.

**Preparation of 1A−3A. 1** (2.50 g, 10.4 mmol) and dibutyltindilaurate (0.5 mL) were dissolved in anhydrous THF (25 mL). Butylisocyanatoacetate (1.89 g, 12 mmol) was added dropwise to this solution with stirring at 0 °C. The mixture was allowed to warm to room temperature, and the stirring was continued for 10 h before ice−water (10 mL) was added. THF was evaporated, and the aqueous residue was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was then evaporated. The residue was eluted through a flash silica gel column by ethyl acetate/petroleum ether (12/88 to 16/84). The product was collected, and the solvent was evaporated. After being vacuum dried at 50 °C for 24 h, **1A** (3.01 g, 73% yield) was obtained as light yellowish oil. IR (neat): 1505, 1600, 1724, 1754, 2253 (weak), 2873, 2959, 3027, 3065, 3353 cm$^{-1}$. $^{1}$H NMR: $\delta$ 7.30 (t, $J = 7.5$, 2H), 6.84 (m, 3H), 5.22 (br, 1H), 4.15 (m, 6H), 3.97 (d, $J = 5.5$, 2H), 3.00 (s, 3H), 2.31 (t, $J = 7.0$, 2H), 1.2−2.8 (m, 8H), 0.97 (br, 3H). $^{13}$C NMR: $\delta$ 170.1 (sp$^2$ −CO), 156.4 (sp$^2$ −CO), 148.8 (sp$^2$ −C), 129.2 (2 sp$^2$ −CH), 118.2 (sp$^2$ −CH), 114.1 (2 sp$^2$ −CH), 78.7 (sp −C), 72.2 (sp −C), 68.8 (sp −C), 65.2 (2 sp$^3$ −$CH_2$), 64.5 (sp −C), 43.0 (sp$^3$ −$CH_2$), 42.6 (sp$^3$ −$CH_2$), 38.6 ($CH_3$), 30.4 (sp$^3$ −$CH_2$), 28.0 (sp$^3$ −$CH_2$), 24.5 (sp$^3$ −$CH_2$), 19.0 (sp$^3$ −$CH_2$), 18.8 (sp$^3$ −$CH_2$), 13.6 ($CH_3$). Anal. Calcd for $C_{23}H_{30}N_2O_4$: C, 69.32; H, 7.59; N, 7.03. Found: C, 68.91; H 7.54; N, 7.38. **2A** was prepared from 6 g (0.02 mol) of **2** instead of **1** and 3.5 g (0.022 mol) of butylisocyanatoacetate in a manner similar to that for **1A** except for the following purification procedure. The crude product was recrystallized out by methanol, and the white solid turned red in room light. After the product was vacuum dried at 50 °C for 12 h, the yield was 97% (8.99 g). The white solid was dissolved in chloroform and cast on a NaCl plate as a neat film for infrared spectroscopy. Mp: 90−93 °C. IR (neat): 723, 747, 1198, 1289, 1459, 1541, 1694, 1757, 2269 (weak), 2953, 3328 cm$^{-1}$. $^{1}$H NMR: $\delta$ 8.13 (d, $J = 8$, 2H), 7.55 (m, 4H), 7.31 (m, 2H), 5.15 (m, 3H), 4.18 (t, $J = 6$, 2H), 4.09 (t, $J = 2$), 3.97 (d, $J = 6$, 2H), 2.30 (t, $J = 6$, 2H), 1.55 (m, 8H), 0.95 (t, $J = 7$, 3H). $^{13}$C NMR: $\delta$ 170.6 (sp$^2$ −CO), 156.8 (sp$^2$ −CO), 140.2 (2 sp$^2$ −C), 126.4 (2 sp$^2$ −CH), 123.7 (2 sp$^2$ −C), 120.8 (2 sp$^2$ −CH), 120.0 (2 sp$^2$ −CH), 109.15 (2 sp$^2$ −CH), 80.4 (sp −C), 70.5 (sp −C), 69.3 (sp −C), 65.7 (sp$^3$ −$CH_2$), 65.4 (sp$^3$ −$CH_2$), 64.9 (sp −C), 43.1 (sp$^3$ −$CH_2$), 34.6 (sp$^3$ −$CH_2$), 33.3 (sp$^3$ −$CH_2$), 30.9 (sp$^3$ −$CH_2$), 28.4 (sp$^3$ −$CH_2$), 24.9 (sp$^3$ −$CH_2$), 19.5 (sp$^3$ −$CH_2$), 19.3 (sp$^3$ −$CH_2$), 14.1 ($CH_3$). Anal. Calcd for $C_{28}H_{30}N_2O_4$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.22; H, 6.86; N, 6.13. **3A** was prepared from 4.56 g (0.015 mol) of **3** instead of **1** and 2.7 g (0.017 mol) of butylisocyanatoacetate in a manner similar to that for **1A** except for the following purification procedure. The crude product was crystallized by ethyl ether and petroleum ether as the white solid turned red in room light. After the product was vacuum dried at room temperature for 12 h, the yield was 99% (6.84 g). Mp: 45−46 °C. IR (KBr): 695, 752, 1245, 1318, 1538, 1695, 1734, 2253 (weak), 2963, 3338 cm $^{-1}$. $^{1}$H NMR: $\delta$ 7.34 (m, 4H), 7.08 (m, 6H), 5.20 (br, 1H), 4.50 (s, 2H), 4.18 (m, 4H), 3.98 (d, $J = 6$, 2H), 2.32 (t, $J = 7$, 2H), 1.55 (m, 8H), 0.97 (t, $J = 7$, 3H). $^{13}$C NMR: $\delta$ 170.6 (sp$^2$ −CO), 156.9 (sp$^2$ −CO), 147.7 (2 sp$^2$ −C), 129.7(4 sp$^2$ −CH), 122.7 (2 sp$^2$ −CH), 121.6 (4 sp$^2$ −CH), 79.5 (sp −C), 72.9 (sp −C), 69.4 (sp −C), 65.7 (2 sp −$CH_2$), 65.0 (sp −C), 43.2 (2 sp$^3$ −$CH_2$), 31.4 (sp$^3$ −$CH_2$), 28.5 (sp$^3$ −$CH_2$), 25.0 (sp$^3$ −$CH_2$), 19.5 (sp$^3$ −$CH_2$), 19.4 (sp$^3$ −$CH_2$), 14.1 ($CH_3$). Anal. Calcd for $C_{28}H_{32}N_2O_4$: C, 73.02; H, 7.00; N, 6.08. Found: C, 72.41; H, 6.96; N, 6.05.

**Preparation of 1B, 1C, and 1E.** 2-Ethylhexylglycinate (3.69 g, 19.7 mmol) was dissolved in 30 mL of anhydrous chloroform (30 mL). Triphosgene (1.96 g, 6.6 mmol) was added to this solution with stirring. Triethylamine (5.0 mL) was added dropwise to this stirred mixture. (A water bath may be needed to keep the temperature below 30 °C.) The reaction mixture was refluxed for 2 h before **1** (1.99 g, 8.2 mmol) and dibutyltindilaurate (5.73 g, 9.075 mmol) were added. The stirring was continued for 10 h at 50 °C. The solvent was evaporated, and the residue was redissolved in hexane. The resulting solution was filtered, and the solid was washed several times with hexane. The filtrate was collected, and the solvent was evaporated. The residue was eluted through a flash silica gel column by ethyl acetate/petroleum ether (16/84). The product was collected, and the solvent was removed. After being vacuum dried at 50 °C for 24 h, **1B** (2.50 g, 67% yield) was obtained as light yellowish oil. IR (neat): 1506, 1600, 1727, 2253 (weak), 2873, 2931, 2959, 3027, 3353 cm$^{-1}$. $^{1}$H NMR (250 MHz): $\delta$ 7.29 (t, $J = 7.5$, 2H), 6.85 (m, 3H), 5.20 (br, 1H), 4.09 (m, 6H), 3.97 (d, $J = 5.5$, 2H), 3.00 (s, 3H), 2.31 (t, $J = 7.0$, 2H), 1.5−1.8 (m, 5H), 1.3 (m, 8H), 0.91 (t, $J = 7.5$, 3H). $^{13}$C NMR (250 MHz): $\delta$ 170.44 (sp$^2$ −CO), 156.61 (sp$^2$ −CO), 149.04 (sp$^2$ −C), 129.29 (sp$^2$ −CH), 118.49 (sp$^2$ −CH), 114.36 (sp$^2$ −CH), 78.94 (sp −C), 72.38 (sp −C), 69.00 (sp −C), 68.03 (sp$^3$ −$CH_2$), 65.48 (sp −C), 64.78 (sp$^3$ −$CH_2$), 43.21 (sp$^3$ −$CH_2$), 42.85 (sp$^3$ −$CH_2$), 38.89 ($CH_3$), 38.85 (sp$^3$ −CH), 30.44 (sp$^3$ −$CH_2$), 29.04 (sp$^3$ −$CH_2$), 28.20 (sp$^3$ −$CH_2$), 24.73 (sp$^3$ −$CH_2$), 23.82 (sp$^3$ −$CH_2$), 23.10 (sp$^3$ −$CH_2$), 19.03 (sp$^3$ −$CH_2$), 14.21 ($CH_3$), 11.12 ($CH_3$). Anal. Calcd for $C_{27}H_{38}N_2O_4$: C, 71.33; H, 8.43; N, 6.16. Found: C, 71.52; H 8.48; N, 6.14. **1C** was prepared from 4.26 g (20 mmol) of menthylglycinate instead of 2-ethylhexylglycinate, 2.08 g (7 mmol) of triphosgene, and 2.41 g (10 mmol) of **1** via a procedure similar to that for **1B**. The desired product was obtained in 83% yield. The white solid was dissolved in chloroform and cast on a NaCl plate as a neat film for infrared spectroscopy. IR (neat): 1506, 1601, 1729, 2254 (weak), 2870, 2927, 2955, 3341 cm$^{-1}$. $^{1}$H NMR: $\delta$ 7.30

(t, $J$ = 8.0, 2H), 6.86 (m, 3H), 5.24 (br, 1H), 4.79 (dt, $J$ = 4.5, 11, 1H), 4.12 (m, 4H), 3.96 (d, $J$ = 5.5, 2H), 3.00 (s, 3H), 2.32 (t, $J$ = 6.5, 1H), 0.7−2.1 (m). $^{13}$C NMR: $\delta$ 169.8 (sp$^2$ −CO), 156.6 (sp$^2$ −CO), 149.0 (sp$^2$ −C), 129.3 (2 sp$^2$ −CH), 118.5 (sp$^2$ −CH), 114.4 (2 sp$^2$ −CH), 78.9 (sp −C), 75.8 (sp$^3$ −CH), 72.4 (sp −C), 69.0 (sp −C) 65.5 (sp −C), 64.7 (sp$^3$ −CH$_2$), 47.1 (sp$^3$ −CH), 43.2 (sp$^3$ −CH$_2$), 43.0 (sp$^3$ −CH$_2$), 40.9 (sp$^3$ −CH$_2$), 38.9 (CH$_3$), 34.3 (sp$^3$ −CH$_2$), 31.5 (sp$^3$ −CH), 28.2 (sp$^3$ −CH$_2$), 26.4 (sp$^3$ −CH), 24.7 (sp$^3$ −CH$_2$), 23.6 (sp$^3$ −CH$_2$), 22.1 (CH$_3$), 20.9 (CH$_3$), 19.0 (sp$^3$ −CH$_2$), 16.5 (CH$_3$). Anal. Calcd for $C_{29}H_{40}N_2O_4$: C, 72.47; H, 8.39; N, 5.83; Found: C, 72.41; H, 9.14; N, 5.69. **1E** was prepared from 2.48 g (10.35 mmol) of L-glutamic acid diethylester hydrochloride instead of 2-ethylhexylglycinate, 1.13 g (3.80 mmol) of triphosgene, and 1.25 g (5.18 mmol) of **1** via a procedure similar to that for **1B** except for the following purification procedure. After being washed with hexane, the solid was dissolved in $CH_2Cl_2$ and extracted with water (3 × 100 mL). The combined organic layer was dried over $MgSO_4$, and the solvent was evaporated, leaving an organic viscous residue. The residue was eluted through a flash silica gel column by ethyl acetate/petroleum ether (30/70 to 35/65). The product was collected and crystallized as the solvent was removed. After being vacuum dried at 50 °C for 24 h, the desired product (1.85 g, 87%) was obtained as a white solid. The white solid was dissolved in chloroform and cast on a NaCl plate as a neat film for infrared spectroscopy. Mp: 79.6 °C. IR (neat): 1505, 1530, 1600, 1724, 2254 (weak), 2977, 3330 cm$^{-1}$: $^1$H NMR: $\delta$ 7.26 (m, 2H), 6.84 (m, 3H), 5.29 (br, 1H), 4.24 (m, 1H), 4.11 (m, 6H), 2.96 (s, 3H), 2,38 (m, 2H), 2.27 (t, $J$ = 6.9, 2H), 2.15 (m, 1H), 197 (m, 1H), 1.62 (m, 4H), 1.25 (m, 6H). $^{13}$C NMR: $\delta$ 173.1 (sp$^2$ −CO), 172.4 (sp$^2$ −CO), 156.5 (sp$^2$ −CO), 149.2 (sp$^2$ −C), 129.6 (2sp$^2$ −CH), 118.9 (sp$^2$ −CH), 114.7 (2sp$^2$ −CH), 79.2 (sp −C), 72.6 (sp −C), 69.3 (sp −C), 65.7 (sp$^3$ −CH$_2$), 65.0 (sp −C), 62.1 (sp$^2$ −CH$_2$), 61.1 (sp$^2$ −CH$_2$), 53.7 (sp$^3$ −CH), 43.5 (sp$^3$ −CH$_2$), 39.2 (CH$_3$), 30.7 (sp$^3$ −CH$_2$), 28.4 (sp$^3$ −CH$_2$), 28.1 (sp$^3$ −CH$_2$), 25.0 (sp$^3$ −CH$_2$), 19.4 (sp$^3$ −CH$_2$), 14.6 (2CH$_3$). Anal. Calcd for $C_{26}H_{34}N_2O_6$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.54; H, 7.43; N, 6.02.

**Preparation of 4A−4C. 1A** (0.55 g, 1.38 mmol) was dissolved in DMF (5 mL). TCNE (0.21 g, 1.64 mmol) was added to the solution with stirring. The stirring was continued for 12 h. Water (50 mL) and acetone (50 mL) were added to the mixture to bring about a precipitation. The resulting red precipitate was collected by vacuum filtration and was reprecipitated in hexane from a $CH_2Cl_2$ solution. After being vacuum dried at 50 °C for 24 h, **4A** (0.38 g, 55% yield) was obtained as reddish orange powder. Mp: 109−110 °C. IR (neat): 1496, 1543, 1607, 1689, 1753, 2217, 2959, 3318 cm$^{-1}$. Raman: 1458 (C═C), 1494 (C═C), 1536 (C═C), 2118 (weak, C≡C of partial polymer), 2218 (C≡N), 2258 (C≡C of monomer) cm$^{-1}$. $^1$H NMR: $\delta$ 8.09 (d, $J$ = 7.5, 2H), 6.85 (d, $J$ = 7.5, 2H), 5.17 (br, 1H), 4.27 (s, 2H), 4.15 (m, 4H), 3.94 (d, $J$ = 5.5, 2H), 3.23 (s, 3H), 2.31 (t, $J$ = 7.0, 2H), 1.66 (m, 6H), 1.37 (m, 2H), 0.93 (t, $J$ = 7.5, 3H). $^{13}$C NMR: $\delta$ 170.3 (sp$^2$ −CO), 156.6 (sp$^2$ −CO), 154.1 (sp$^2$ −C), 138.4 (sp$^2$ −C), 133.0 (2 sp$^2$ −CH), 118.5 (sp$^2$ −C), 114.4 (sp −CN), 113.6 (sp −CN), 113.4 (sp −CN), 113.2 (2 sp$^2$ −CH), 80.9 (sp$^2$ −C), 80.4 (sp −C), 70.4 (sp −C), 69.2 (sp −C), 65.5 (sp$^3$ −CH$_2$), 64.8 (sp$^3$ −CH$_2$), 64.7 (sp −C), 42.9 (2 sp$^3$ −CH$_2$), 39.0 (CH$_3$), 30.7 (sp$^3$ −CH$_2$), 28.2 (sp$^3$ −CH$_2$), 24.6 (sp$^3$ −CH$_2$), 19.2 (sp$^3$ −CH$_2$), 19.0 (sp$^3$ −CH$_2$), 13.8 (CH$_3$). $\lambda_{max}$ (CHCl$_3$) = 499 nm. Anal. Calcd for $C_{28}H_{29}N_5O_4$: C, 67.32; H, 5.85; N, 14.02. Found: C, 67.62; H 5.86; N, 13.76. **4B** was prepared from 2.15 g (4.73 mmol) of **1B** instead of **1A** and 0.73 g (5.68 mmol) of TCNE in a manner similar to that for **4A**. The desired product was obtained in 82% yield. Mp: 100.5−101.5 °C. IR (neat): 1495, 1542, 1606, 1688, 1753, 2216, 2259 (weak), 2864, 2930, 2959, 3323 cm$^{-1}$. Raman: 1455 (C═C), 1494 (C═C), 1536 (C═C), 2072 (weak, C≡C of partial polymer), 2216 (C≡N), 2260 (C≡C of monomer) cm$^{-1}$. $^1$H NMR: $\delta$ 8.09 (d, $J$ = 7.5, 2H), 6.83 (d, $J$ = 7.5, 2H), 5.19 (br, 1H), 4.27 (s, H), 4.11 (m, 4H), 3.95 (d, $J$ = 5.5, 2H), 3.23 (s, 3H), 2.31 (t, $J$ = 6.5, 2H), 1.5−1.8 (m, 5H), 1.3 (m, 8H), 0.88 (t, $J$ = 7.5, 3H). $^{13}$C NMR: $\delta$ 170.4 (sp$^2$ −CO), 156.6 (sp$^2$ −CO), 154.1 (sp$^2$ −C), 138.4 (sp$^2$ −C), 133.0 (2 sp$^2$ −CH), 118.5 (sp$^2$ −C), 114.4 (sp −CN), 113.6 (sp −CN), 113.4 (sp −CN), 113.2 (2 sp$^2$ −CH), 80.9 (sp$^2$ −C), 80.4 (sp −C), 70.4 (sp −C), 69.2 (sp −C), 68.1 (sp$^3$ −CH$_2$), 64.8 (2 sp$^3$ −CH$_2$), 64.7 (sp −C), 42.9 (2 sp$^3$ −CH$_2$), 39.0 (CH$_3$), 38.8 (sp$^3$ −CH), 30.4 (sp$^3$ −CH$_2$), 29.0 (sp$^3$ −CH$_2$), 28.2 (sp$^3$ −CH$_2$), 24.6 (sp$^3$ −CH$_2$), 23.8 (sp$^3$ −CH$_2$), 23.1 (sp$^3$ −CH$_2$), 19.0 (sp$^3$ −CH$_2$), 14.2 (CH$_3$), 11.1 (CH$_3$). $\lambda_{max}$ (CHCl$_3$) = 499 nm. Anal. Calcd for $C_{32}H_{37}N_5O_4$: C, 69.16; H, 6.71; N, 12.61. Found: C, 69.44; H, 6.42; N, 12.72. **4C** was prepared from 3.22 g (6.7 mmol) of **1C** instead of **1A** and 1.03 g (8 mmol) of TCNE via a manner similar to for **4A**. The desired product was obtained in 60% yield. Mp: 82−83 °C. IR (neat): 1494, 1605, 1723, 2219, 2256 (weak), 2870, 2955, 3088, 3403 cm$^{-1}$. Raman: 1456 (C═C), 1494 (C═C), 1538 (C═C), 2122 (weak, C≡C of partial polymer), 2218 (C≡N), 2260 (C≡C of monomer) cm$^{-1}$. $^1$H NMR: (250 MHz) $\delta$ 8.08 (d, $J$ = 7.5, 2H), 6.84 (d, $J$ = 7.5, 2H), 5.17 (br, 1H), 4.74 (dt, $J$ = 4.5, 11, 1H), 4.27 (s, 2H), 4.08 (t, $J$ = 6, 2H), 3.92 (d, $J$ = 5.5, 2H), 3.23 (s, 3H), 2.30 (t, $J$ = 6.5, 2H), 1.90 (m, 1H), 1.2−1.8 (m, 9H), 0.8−1.1 (m, 9H), 0.74 (d, $J$ = 7.5, 3H). $^{13}$C NMR (250 MHz): $\delta$ 169.6 (sp$^2$ −CO), 156.4 (sp$^2$ −CO), 154.1 (sp$^2$ −C), 138.3 (sp$^2$ −C), 132.8 (2 sp$^2$ −CH), 118.4 (sp$^2$ −C), 114.4 (sp −CN), 113.5 (sp −CN), 113.4 (sp −CN), 113.2 (2 sp$^2$ −CH), 80.8 (sp$^2$ −C), 80.3 (sp −C), 75.8 (sp$^2$ −CH), 70.5 (sp −C), 69.2 (sp −C), 64.8 (sp$^3$ −CH$_2$), 64.6 (sp −C), 47.1 (sp$^3$ −CH), 43.0 (sp$^3$ −CH$_2$), 42.8 (sp$^3$ −CH$_2$), 40.9 (sp$^3$ −CH$_2$), 38.8 (CH$_3$), 34.2 (sp$^3$ −CH$_2$), 31.5 (sp$^3$ −CH), 28.2 (sp$^3$ −CH$_2$), 26.5 (sp$^3$ −CH), 24.6 (sp$^3$ −CH$_2$), 23.7 (sp$^3$ −CH$_2$), 22.0 (CH$_3$), 20.7 (CH$_3$), 19.0 (sp$^3$ −CH$_2$), 16.5 (CH$_3$). $\lambda_{max}$ (CHCl$_3$) = 500 nm. Anal. Calcd for $C_{34}H_{39}N_5O_4$: C, 70.19; H, 6.76; N, 12.04. Found: C, 70.00; H, 6.45; N, 12.09.

**Polymerization.** Polymerization of polymerizable solids (except for **1A**) was carried out by preparing evacuated ampules under N$_2$ atmosphere. Subsequently, the solid samples of diacetylenes were exposed to 50 Mrad of $\gamma$-radiation from $^{60}$Co. The resulting polymer was purified by either reprecipitation or Soxhlet extraction, followed by drying at 50 °C for 24 h under vacuum. The purification method and polymerization yield are summarized in Table 2. All soluble PDAs were dissolved in chloroform and cast on NaCl plates as neat films for infrared spectroscopy. Polymerization of **1A** is as follows: Polymerizable **1A** (0.389 g) was obtained from a crystallization of pure **1A** in ether−petroleum ether (1:2) at −78 °C. The solvent was evaporated quickly by a rotary evaporator without warming the solution. The resulting partially polymerized pink solid was exposed to 46 Mrad (dose rate = 0.5 Mrad/h) of $\gamma$-irradiation from $^{60}$Co while it was packed in dry ice. The polymer was purified by precipitation twice in MeOH from $CH_2Cl_2$ solution. After being vacuum dried at 50 °C for 24 h, **PDA-1A** (0.152 g, 39% yield) was obtained as red fibrous solid. IR (neat): 1507, 1600, 1697, 1725, 1754, 2134 (weak), 2873, 2958, 3061, 3333 cm$^{-1}$. Raman: 1514 (C═C), 2114 (C≡C) cm$^{-1}$. $^1$H NMR (500 MHz): $\delta$ 7.09 (br, 2H), 6.58 (br, 3H), 5.40 (br, 1H), 3.6−4.3 (br, m, 8H), 2.80 (br, 3H), 2.31 (br, 1H), 1.2−2.9 (br, m, 8H), 0.94 (br, 3H). $^{13}$C NMR (500 MHz): $\delta$ 170.5 (sp$^2$ −CO), 156.9 (sp$^2$ −CO), 149.6 (sp$^2$ −C), 131.4 (sp$^2$ −C), 129.2 (2 sp$^2$ −CH), 128.5 (sp$^2$ −C), 116.6 (sp$^2$ −CH), 112.5 (2 sp$^2$ −CH), 100.7 (sp −C), 99.5 (sp −C), 65.4 (2 sp$^3$ −CH$_2$), 55.2 (sp$^3$ −CH$_2$), 42.9 (sp$^3$ −CH$_2$), 38.4 (CH$_3$), 35.3 (sp$^3$ −CH$_2$), 30.8 (sp$^3$ −CH$_2$), 28.7 (sp$^3$ −CH$_2$), 25.1 (sp$^3$ −CH$_2$), 19.3 (sp$^3$ −CH$_2$), 13.8 (CH$_3$). $\lambda_{max}$ (CHCl$_3$) = 473 nm. Anal. Calcd for $(C_{23}H_{30}N_2O_4)_n$: C, 69.32; H, 7.59; N, 7.03. Found: C, 70.13; H 7.81; N, 6.89. **PDA-1C.** IR (neat): 1507, 1600, 1727, 2216, 2869, 2953, 3336 cm$^{-1}$. Raman: 1516 (C═C), 2118 (C≡C) cm$^{-1}$. $^1$H NMR (500 MHz): $\delta$ 7.09 (br, 2H), 6.59 (br, 3H), 5.36 (br, 1H), 4.74 (br, 1H), 3.94 (br, m, 6H), 2.80 (s, 3H), 2.31 (br, 1H), 0.7−2.0 (br, m). $^{13}$C NMR (500 MHz): $\delta$ 170.0 (sp$^2$ −CO), 156.8 (sp$^2$ −CO), 149.4 (sp$^2$ −C), 131.2 (sp$^2$ −C), 129.2 (2 sp$^2$ −CH), 128.7 (sp$^2$ −C), 116.6 (sp$^2$ −CH), 112.5 (2 sp$^2$ −CH), 101.0 (sp −C), 99.5 (sp −C), 75.7 (sp$^3$ −CH), 65.3 (sp$^3$ −CH$_2$), 55.2 (sp$^3$ −CH$_2$), 47.2 (sp$^3$ −CH), 43.1 (sp$^3$ −CH$_2$), 41.1 (sp$^3$ −CH$_2$), 38.4 (CH$_3$), 35.3 (sp$^3$ −CH$_2$), 34.4 (sp$^3$ −CH$_2$), 31.6 (sp$^3$ −CH), 28.7 (sp$^3$ −CH$_2$), 26.6 (sp$^3$ −CH), 25.1 (sp$^3$ −CH$_2$), 23.8 (sp$^3$ −CH$_2$), 22.2 (CH$_3$), 20.9 (CH$_3$), 16.6 (CH$_3$). $\lambda_{max}$ (CHCl$_3$) = 469 nm. $\lambda_{max}$ (film) = 470 nm. Anal. Calcd for $(C_{29}H_{40}N_2O_4)_n$: C, 72.47; H, 8.39; N, 5.83; Found: C, 71.88; H 8.23; N, 5.74. **PDA-1E.** IR (neat): 1507, 1600, 1693, 1733, 2943, 3327 cm$^{-1}$. Raman: 1519 (C═C), 2117 (C≡C) cm$^{-1}$. $^1$H NMR: $\delta$ 7.11 (br, 2H), 6.59 (br, 3H), 5.60 (br, 1H), 4.33 (br, 1H), 4.14 (br, 6H), 2.82 (s, 3H), 1.22−2.40 (br, 15H). $^{13}$C NMR: $\delta$ 172.9 (sp$^2$ −CO), 172.4 (sp$^2$ −CO), 156.6 (sp$^2$ −CO), 149.6 (sp$^2$ −C), 131.3 (sp$^2$ −C), 129.3 (2sp$^2$ −CH), 129.0 (sp$^2$ −C), 116.8 (sp$^2$ −CH), 112.7 (2sp$^2$ −CH), 101.5 (sp −C), 100.0 (sp −C), 65.5 (sp$^3$ −CH$_2$), 61.8 (sp$^3$ −CH$_2$), 60.9 (sp$^3$ −CH$_2$), 55.4 (sp$^3$ −CH), 53.8 (sp$^3$ −CH$_2$), 38.5 (CH$_3$), 35.4 (sp$^3$ −CH$_2$), 28.8 (sp$^3$ −CH$_2$), 28.0 (sp$^3$ −CH$_2$), 25.2 (sp$^3$ −CH$_2$), 14.5 (CH$_3$). $\lambda_{max}$ (CHCl$_3$) = 465 nm. $\lambda_{max}$ (film) = 479 nm. Anal. Calcd for $(C_{26}H_{34}N_2O_6)_n$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.36; H, 7.28; N, 6.02. **PDA-2A.** IR (KBr): 721, 748, 1196, 1693, 1459, 1757, 2953, 3427 cm$^{-1}$. Raman: 1509 (C=C), 2112 ($C\equiv C$) cm$^{-1}$. Anal. Calcd for $(C_{28}H_{32}N_2O_4)_n$: C, 73.02; H, 7.00; N, 6.08. Found: C, 72.41; H, 6.96; N, 6.05. **PDA-3A.** IR (neat): 721, 748, 1196, 1459, 1693, 1757, 2953, 3427 cm$^{-1}$. Raman: 1490 (C=C), 2105 ($C\equiv C$) cm$^{-1}$. $^1$H NMR (250 MHz): $\delta$ 7.30 (m, 2H), 6.97 (br, 4H), 6.74 (br, 4H), 5.26 (br, 1H), 4.62 (s, 2H), 4.04 (m, 4H), 3.98 (br, 2H), 2.24 (br, 2H), 1.53 & 1.27 (m, 8H), 0.85 (t, $J$ = 7, 3H). $^{13}$C NMR (500 MHz): $\delta$ 170.7 (sp$^2$ −CO), 157.1 (sp$^2$ −CO), 147.8 (2 sp$^2$ −C), 131.4 (sp$^2$ −C), 129.9 (2 sp$^2$ −CH), 129.4 (4 sp$^2$ −CH), 121.7 (sp$^2$ −C), 121.1 (2 sp$^2$ −CH), 121.6 (4 sp$^2$ −CH), 101.0 (sp −C), 99.5 (sp −C), 65.4 (2 sp$^3$ −CH$_2$), 55.4 (2 sp$^3$ −CH$_2$), 43.0 (sp$^3$ −CH$_2$), 35.4 (sp$^3$ −CH$_2$), 30.9 (sp$^3$ −CH$_2$), 28.6 (sp$^3$ −CH$_2$), 25.2 (sp$^3$ −CH$_2$), 19.4 (sp$^3$ −CH$_2$), 19.4 (sp$^3$ −CH$_2$), 14.1 (CH$_3$). Anal. Calcd for $(C_{28}H_{32}N_2O_4)_n$: C, 73.02; H, 7.00; N, 6.08. Found: C, 73.13; H, 7.39; N, 6.11. **PDA-4A.** IR (KBr): 1496, 1542, 1610, 1692, 1755, 2222, 2962, 3325 cm$^{-1}$. Raman (KBr): 1488 (C=C), 2104 ($C\equiv C$) cm$^{-1}$. Anal. Calcd for $(C_{28}H_{29}N_5O_4)_n$: C, 67.32; H, 5.85; N, 14.02. Found: C, 65.55; H 5.82; N, 13.18. **PDA-4B.** IR (KBr): 1495, 1542, 1606, 1690, 1720, 1753, 2216, 2859, 2929, 2958, 3319, 3427 cm$^{-1}$. Raman: 1455 (C=C), 1486 (C=C), 2080 ($C\equiv C$) cm$^{-1}$. Anal. Calcd for $C_{32}H_{37}N_5O_4$: C, 69.16; H, 6.71; N, 12.61. Found: C, 68.53; H, 6.72; N, 12.59. **PDA-4C.** IR (KBr): 1495, 1607, 1697, 2216, 2868, 2929, 2954, 3410 cm$^{-1}$. Raman: 1499 (C=C), 2106 ($C\equiv C$) cm$^{-1}$. Anal. Calcd for $(C_{34}H_{39}N_5O_4)_n$: C, 70.19; H, 6.76; N, 12.04. Found: C, 69.53; H, 6.79; N, 11.81.

**Postpolymerization Functionalization.** *Tricyanovinylation:* ***PDA-1A−TCV*** *and* ***PDA-1C−TCV*****.** **PDA-1A** (80 mg, 0.20 mmol) dissolved in DMF (8 mL) was reacted with TCNE (39 mg, 0.30 mmol). The resulting polymer was precipitated twice in MeOH (150 mL) from DMF solutions. After being vacuum dried at 50 °C for 24 h, the product (80 mg) was obtained as dark red solid. IR (neat): 1494, 1605, 1723, 2216, 2871, 2935, 2959, 3351 cm$^{-1}$. Raman: 1506 (C=C), 2116 ($C\equiv C$) cm$^{-1}$. $^1$H NMR: $\delta$ 7.7−8.1 (br, 0.65H), 6.9−7.2 (br, 0.79H), 6.2−6.8 (br, 1.80H), 5.5−5.9 (br, 1H), 3.6−4.4 (br, m, 8H), 2.7−3.1 (br, 3H), 2.3−3.6 (br, 1H), 1.2−2.9 (br, m), 0.94 (br, 3H). $\lambda_{max}$ (CHCl$_3$) = 499 nm. Anal. Calcd for $[(C_{23}H_{30}N_2O_4)_{0.55}(C_{28}H_{29}N_5O_4)_{0.45}]_n$: C, 68.30; H, 6.71; N, 10.57. Found: C, 66.53; H 6.37; N, 12.14 (sample contained some DMF). **PDA-1C−TCV** was prepared via a procedure similar to that above, but using 0.09 g (0.187 mmol) of **PDA-1C** instead of **PDA-1A**. IR (neat): 1495, 1606, 1719, 2216, 2869, 2954, 3336 cm$^{-1}$. Raman: 1504 (C=C), 2116 ($C\equiv C$) cm$^{-1}$. $^1$H NMR: $\delta$ 7.7−8.1 (br, 1.55H), 6.9−7.2 (br, 0.83H), 6.2−6.8 (br, 1.97H), 5.5−5.9 (br, 1H), 4.74 (br, 1H), 3.5−4.3 (br, m 6H), 0.7−3.1 (br, m). $\lambda_{max}$ (CHCl$_3$) = 504 nm. $\lambda_{max}$ (film) = 494 nm. Anal. Calcd for $[(C_{29}H_{40}N_2O_4)_{0.55}(C_{34}H_{39}N_5O_4)_{0.45}]_n$: C, 71.34; H, 7.58; N, 8.92. Found: C, 71.34; H, 7.92; N, 8.81.

*Diazotization:* ***PDA-5A.*** A diazonium salt of 4-aminobenzoic acid was prepared by adding an aqueous solution of sodium nitrite (0.08 g, 1.578 mmol in 0.1 mL of water) dropwise into a solution of 4-aminobenzoic acid (0.1371 g, ca. 1 mmol) in a homogeneous mixture of 0.1 mL of sulfuric acid and 2 mL of glacial acetic acid. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by the addition of 0.1 g of sulfamic acid in a suitable amount of water. The diazonium salt solution was added dropwise into a solution of **PDA-1A** (0.1892 g, 0.4 mmol) in 50 mL of N,N′-dimethylformamide at 0 °C. The solution was stirred at 0 °C for 12 h. **PDA-5A** was obtained by precipitation of the above solution in water and was washed with plenty of water until neutral stage was achieved. The polymer was further purified by extraction several times with chloroform. IR (KBr): 704, 758, 788, 833, 873, 938, 1067, 1139, 1199, 1374, 1509, 1599, 1719, 2959, 3427 cm$^{-1}$. Raman: 1447 (N=N), 1510 (C=C), 2118 ($C\equiv C$) cm$^{-1}$. $^1$H NMR: $\delta$ 8.00 (br, 2H), 7.60 (br, 4H), 7.34 (br, 2H), 7.10 (br, 2H), 6.76 (br, 3H), 3.66−3.99 (br, m, 8H), 3.36 (br, 3H), 2.50−2.52 (br, m, 5H), 1.15−1.46 (br, m, 8H), 0.80 (br, 3H). $\lambda_{max}$ (DMF) = 432 nm.

**Acknowledgment.** The partial funding from the Office of Naval Research under the Multidisciplinary University Research Initiative is gratefully acknowledged. The 500 MHz NMR spectrometer used in this work was purchased with funds partially furnished by the National Science Foundation under Grant NSF-DMR 9402529. L.L. acknowledges the SBIR grant (No. DMI-9510017) from the National Science Foundation. The authors thank Ms. M. Montesalvo for furnishing access to the $^{60}$Co source. We also thank Prof. Bruce M. Foxman (Brandeis University) for collecting the X-ray diffraction data of **4B**.

**Supporting Information Available:** Preparation and Characterization of 9-(*N*,*N*-methylphenylamino)-5,7-nonadiyn-1-ol (**1**), 9-(*N*-carbazolyl)-5,7-nonadiyn-1-ol (**2**), 9-(*N*,*N*-diphenylamino)-5,7-nonadiyn-1-ol (**3**), and **1D**. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) (a) Sauteret, C.; Hermann, J. P.; Frey, R.; Predere, F.; Ducuing, J. R.; Baughman, H.; Chance, R. R. *Phys. Rev. Lett.* **1976**, *36*, 956. (b) Bloor, D.; Chance, R. R. *Polydiacetylenes*; Martinus Nijhoff: Boston, 1985; p 239. (c) Sandman, D. J. *Crystallographically Ordered Polymers*; ACS Symposium Series 337; American Chemical Society: Washington, D.C., 1987. (d) Nakanishi, H.; Matsuda, H.; Kato, M. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 77. (e) Sandman, D. J. *Trends Polym. Sci.* **1994**, *2*, 44. (f) Sandman, D. J. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 2, p 1468.

(2) (a) Patel, G. N. *Polym. Prepr.* **1978**, *19*, 15. (b) Patel, G. N. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 607. (c) Hankin, S.; Sandman, D. J.; Yost, E. A.; Stark, T. J. *Synth. Met.* **1993**, *49*, 281.

(3) (a) Kim, W. H.; Kodali, N. B.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1994**, *27*, 1819. (b) Kim, W. H.; Bihari, B.; Moody, R, Kodali, N. B.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1995**, *28*, 642. (c) Tripathy, S. K.; Kim, W. H.; Bihari, B.; Moody, R.; Kumar, J. *Synth. Met.* **1995**, *71*, 1675. (d) Tripathy, S. K.; Kim, W. H.; Masse, C.; Jiang, X. L.; Kumar J. *Nonlinear Opt.* **1996**, *15*, 111. (e) Cheong, D.-W.; Kim, W. H.; Samuelson, L. A.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1996**, *29*, 1416.

(4) Kim, W. H.; Jiang, X. L.; Kumar, J.; Tripathy, S. K. *Pure Appl. Chem.* **1995**, *67*, 2023.

(5) Sukwattanasinitt, M.; Wang, X.; Li, L.; Jiang, X. L.; Kumar, J.; Tripathy, S. K.; Sandman, D. J. *Chem. Mater.* **1998**, *10*, 27.

(6) Katz, H. E.; Singer, K. D.; Sohn, J. E.; Dirk, C. W.; King, L. A.; Gordon, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 6561.

(7) (a) Jen, A. K.-Y.; Cai, Y.; Rao, V. P.; Dalton, L. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2711. (b) Jen, A. K.-Y.; Cai, Y.; Drost, K. J.; Liu, Y.-J.; Rao, V. P.; Chen, T.-A.; Mininni, R. M.; Kenney, J. T. *Polym. Mater. Sci. Eng.* **1995**, *72*, 213. (c) Chen, T.; Jen, A. K.-Y.; Cai, Y. *Chem. Mater.* **1996**, *8*, 607.

(8) (a) Genet, J. P.; Kopola, N.; Juge, S.; Ruiz-Montes, J.; Antunes, O. A. C.; Tanier, S. *Tetrahedron Lett.* **1990,** 3136. (b) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1561.

(9) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: New York, 1988; p 150.

(10) Reppe, W. *J. Liebigs Ann. Chem.* **1955**, *596*, 38.

(11) Yee, K. C.; Chance, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 431.

(12) Morrow, M. E.; White, K. M.; Eckhardt, C. J.; Sandman, D. J. *Chem. Phys. Lett.* **1987**, *140*, 263.

(13) Chodkiewicz, W.; Cadiot, P. *C. R. Acad. Sci.* **1955**, *241*, 1055.

(14) Greenwald, R. G.; Pendri, A.; Bolikal, D. *J. Org. Chem.* **1995**, *60*, 331.

(15) McKusick, B. C.; Heckert, R. T.; Cairns, T. L.; Coffman, D. D.; Mower, H. F. *J. Am. Chem. Soc.* **1958**, *80*, 2806.

(16) (a) Huntsman, W. D. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1983; Supplement C, p 963. (b) Hankin, S. H. W.; Sandman, D. J. In *Structure−Property Relations in Polymers*; Urban, M. W., Craver, C. D., Eds.; Advances in Chemistry Series 236; American Chemical Society: Washington, DC, 1993; p 245.

(17) Nogami, T.; Nakano, Y.; Hasegawa, Y.; Shirota. Y.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2110.

(18) Wang, X.; Chen, J.-I.; Marturunkakul, S.; Li, L.; Kumar, J.; Tripathy, S. K. *Chem. Mater.* **1997**, *9*, 45.

(19) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. In *Introduction to Infrared and Raman Spectroscopy*, 3rd ed.; Academic Press: New York, 1990; p 350.

(20) Lee, D.-C.; Sukwattanasinitt, M.; Wang, X.; Li, L.; Kumar, J.; Tripathy, S. K.; Sandman, D. J. *Polym. Prepr.* **1998**, *39*, 554.

(21) Chen, J. I.; Marturunkakul, S.; Li, L.; Kumar, J.; Tripathy, S. K. In *Handbook of Conducting Polymers*; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p 727.

(22) Yoshimura, T. *Phys. Rev. B* **1989**, *40*, 6292.

(23) Günter, P., Huignard, J.-P., Eds. *Photorefractive Materials and Their Applications: I. Topics in Applied Physics;* Springer-Verlag: Berlin, 1988; Vol. 61.

(24) (a) Ducharme, S.; Scott, J. C.; Twieg, R. J.; Moerner, W. E. *Phys. Rev. Lett.* **1991**, *67*, 2590. (b) Moerner, W. E.; Silence, S. M. *Chem. Rev.* **1994**, *94*, 127. (c) Liphardt, M.; Goonesekera, A.; Jones, B. E.; Ducharme, S.; Takacs, J. M.; Zhang, L. *Science* **1994**, *263*, 367. (d) Meerholz, K.; Volodin, B. L.; Sandalphon; Kippelen, B.; Peyghambarian, N. *Nature* **1994**, *371*, 497.

(25) Peng, Z.; Bao, Z.; Yu, L. *J. Am. Chem. Soc.* **1994**, *116*, 6005.

(26) Yu, L.; Chan, W. K.; Peng, Z.; Gharavi, A. *Acc. Chem. Res.* **1996**, *29*, 13.

(27) Li, L.; Chittibabu, K. G.; Kumar, J.; Chen, Z.; Chen, J. I.; Marturunkakul, S.; Kumar, J.; Tripathy, S. K. *Opt. Commun.* **1993**, *2042*, 376.

(28) (a) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166. (b) Kim, D. Y.; Li, L.; Jiang, X. L.; Shivshankar, V.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1995**, *28*, 8835. (c) Jiang, X. L.; Li, L.; Kumar, J.; Kim, D. Y.; Shivshankar, V.; Tripathy, S. K. *Appl. Phys. Lett.* **1996**, *68*, 2618. (d) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136.

(29) Tripathy, S. K.; Kim, D. Y.; Li, L.; Kumar, J. *Chemtech* **1998**, *28*, 34.

MA990776O