Polymer Bulletin 49, 103-110 (2002)

Polymer Bulletin

Diacetylene-containing polymers. XIII. Poly(hexa-2,4-diynylene-1,6-dioxydicinnamates) containing an azo dye, Disperse Red 19

Hirohiko Miura[a] **and Takeshi Ogawa** (✉)

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Apartado Postal 70-360, Ciudad Universitaria, México DF 04510, México.
[a]Present address: Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan
email: ogawa@servidor.unam.mx

Received: 21 May 2002 / Revised version: 9 September 2002 / Accepted: 10 September 2002

Summary

In order to obtain polymers having high second order nonlinear optical susceptibility, a series of novel polymers that contain a diacetylene group in the main chains and a polar chromophore (Disperse Red 19) were synthesized and characterized. These poly(hexa-2,4-diynylene-1,6-dioxydicinnamates) undergo crystallization in dimethylformamide solution, and the polymer crystals were only soluble in N-methylpyrrolidinone. The polymer films could be cross-linked by irradiation of UV light to give completely insoluble materials. Preliminary experiments on second order nonlinear properties of these polymers showed that the *para*-polymer was found to have nonlinear optical coefficients about five times greater than the *meta*-polymer.

Introduction

There are many studies on organic polymers which contain polar dye molecules in main or side chains, and their second order nonlinear optical (2-NLO) properties have been investigated (1-3). The majority of these polymers consist of main chains in which polar dye molecules (chromophores) are attached as pendant groups, and their films are subjected to high electric voltage (poling) in order to orientate the dye molecules. The 2-NLO property determined as second harmonic generation (SHG) of these polymers has been considered to depend mainly on the nature of the dye molecules (hyperpolarizability) and the degree of orientation, and other factors which arise from polymer chains themselves have been neglected. In many so far published articles, therefore, the design of materials is mainly based on the hyperpolarizability of the chromophores, and little has been mentioned on the nature of the polymer main chains. It is obvious that high Tg polymers such as polyamides and polyimides are difficult to respond to poling. Vinyl polymers such as polymethacrylates whose main chains consist of tetra-substituted carbon atoms must have certain difficulty in the orientation of branching chromophores, and they readily return to the original random state when electric field is removed.

Previously, the present authors group has synthesized a variety of polymers that contain diacetylenic groups in the main chains and chromophores in the side chains, so that the polymers can be cross-linked after poling to fix the orientated chromophores (4). Their 2-NLO properties were so different each other depending on the flexibility of main chains (5). The SHG of some of the poly(hexa-2,4-diynylene-1,6-dioxy)dibenzoates containing different chromophores, were very high, probably because of their extremely high orientation efficiency, the order parameters being more than 0.5. Since the chromophores employed were known molecules, the polymer main chain has an important effect on this high poling efficiency (6).

Another important problem of the poled polymers is the relaxation of orientation. In order to avoid this, cross-linking of polymer chains is considered to be one solution, and various cross-linkable groups have been studied. Previously, Dalton and coworkers have reported polymers containing a Disperse Red 19 type chromophore in the side chains, and various cross-linkable groups in the main chain (7). They attributed the difference in SHG property to the high chromophore contents. The polymers previously reported by the present authors (4,5) undergo cross-linking by light thorough their diacetylene groups, and the polymers are converted to thermoset resins under very mild conditions. In this work as a continuation of the previous studies, novel polymers consisting of cinnamate main chains with 2,4-hexadiyne groups and an azo dye molecule (Disperse Red 19) in the side chains were synthesized and characterized.

Experimental

Monomer synthesis

Methyl 4-hydroxycinnamate: 4-Hydroxycinnamic acid (80.0 g, 0.487 mole) was refluxed with 600 ml of methanol in the presence of a catalytic amount of sulfuric acid for 16 h. The solution was concentrated under the reduced pressure and poured into water. The precipitate was recrystallized from methanol, affording 69.3 g (0.389 mole) of methyl 4-hydroxycinnamate (Yield 80%). mp 135–136°C. IR (KBr): 3378 (O-H), 1687(C=O) cm^{-1}.

Methyl 4-propargyloxycinnamate: Methyl 4-hydroxycinnamate (69.3 g, 0.389 mole) and propargyl bromide (0.506 mole) was dissolved in acetone (600 ml) and the solution was refluxed in the presence of potassium carbonate (107.6 g) for 20 h. The precipitate was filtered off, and the solution was evaporated. The residue was dissolved in chloroform and washed with water. The chloroform solution was dried over magnesium sulfate and evaporated. The residue was recrystallized from chloroform to afford 73.7 g (0.341 mole) of methyl 4-propargyloxycinnamate (Yield 88%). mp 67–68°C. IR (KBr): 3254 (H-C≡), 2130 (C≡C), 1698 (C=O) cm^{-1}.

4-Propargyloxycinnamic acid: Methyl 4-propargyloxycinnamate (73.7 g, 0.341 mole) and sodium hydroxide (16.4 g) was refluxed with the 600 ml of a mixed solvent of water and methanol (1:1) for 16 h. The solution was concentrated under the reduced pressure and poured into the water. The solution was acidified by hydrochloric acid. The precipitate was collected by filtration and washed with water. The precipitate was recrystallized from methanol to afford 59.6 g (0.294 mole) of 4-propargyloxycinnamic acid (Yield 86%). mp 179–180°C. IR (KBr): 3274 (H-C≡), 2129(C≡C), 1689(C=O) cm^{-1}.

3-Propargyloxycinnamic acid: 3-Hydroxycinnamic acid (50.0 g, 0.304 mole) and propargyl bromide (0.608 mole) was refluxed with methanol (600 ml) in the presence of potassium carbonate (84.0 g) for 16 h. The precipitate was filtered off, and the solution was evaporated. The residue was dissolved in water and acidified by hydrochloric acid. The precipitate was collected by filtration and washed with water. The precipitate was recrystallized from methanol to afford 53.1 g (0.263 mole) of 3-propargyloxycinnamic acid (Yield 86%). mp 151–152°C. IR (KBr): 3288 (H-C≡), 2117 (C≡C), 1682 (C=O) cm^{-1}.

The ^1H NMR spectra of these novel acids are shown in Fig 1.

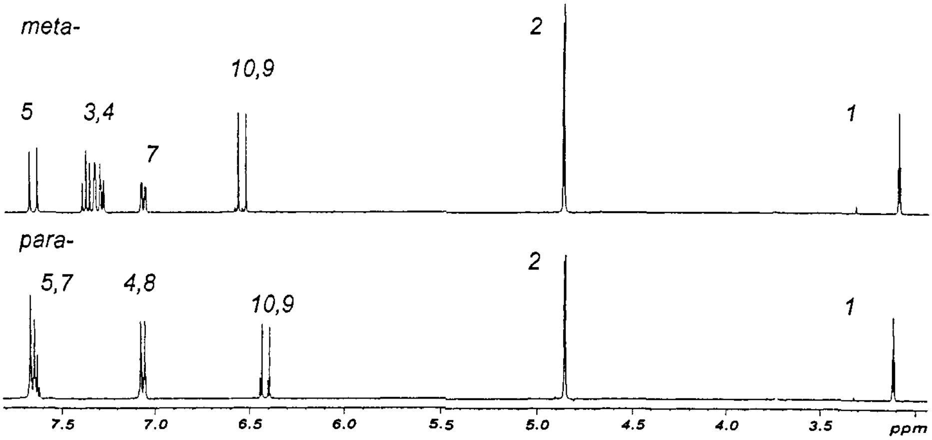


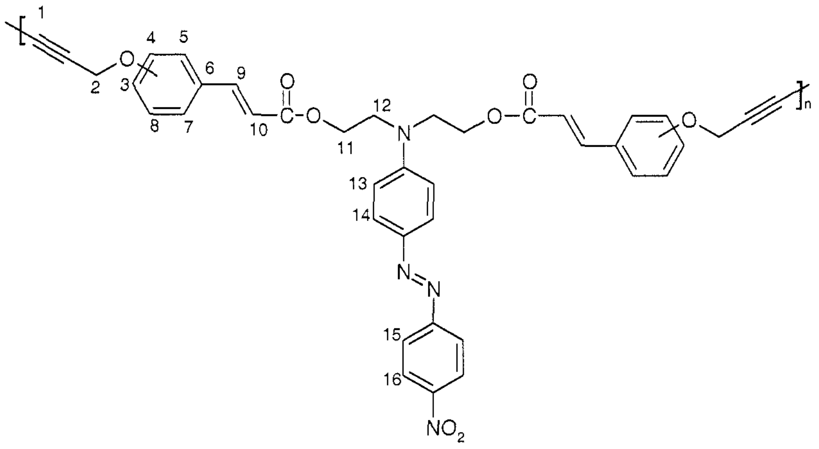
Fig. 1. ^1H NMR spectra of *para-* and *meta-*propargyloxybenzoic acids taken in acetone-*d*. The peak numbers correspond to those of the structure.

N,N-di[2-(4-propargyloxycinnamoyloxy)ethyl]-4-(4'-nitrophenylazo)aniline (1): 4-Propargyloxycinnamic acid (15.0 g, 74.2 mmole) and thionyl chloride (20 ml) was refluxed with dichloromethane (100 ml) for 6 h. After evaporation of solvent and excess thionyl chloride, the residue was recrystallized from *n*-hexane, affording 10.6 g (48.0 mmole) of 4-Propargyloxycinnamoyl chloride (Yield 65%). To a solution of the resulting chloride (10.6 g, 48.0 mmole) in dichloromethane (100 ml) was added triethylamine (7 ml) and *N,N*-di(2-hydroxyethyl)-4-(4'-nitrophenylazo)aniline (4.0 g, 12.1 mmole), and the solution was refluxed for 6 h. Then, methanol was added to the solution, and the solvent was evaporated. The residue was washed with water and recrystallized from butanol to afford 6.9 g (9.9 mmole) of *N,N*-di[2-(4-propargyloxycinnamoyloxy)ethyl]-4-(4'-nitrophenylazo)aniline (Yield 82%). mp 157°C. IR (KBr): 3285 (H-C≡), 3263 (H-C≡), 1715 (C=O), 1699 (C=O)cm^{-1}. Elemental Analysis: Calcd. for $C_{40}H_{34}N_4O_8$ C: 68.76%, H: 4.87%, N: 8.02%, Found: C: 68.40%, H: 4.32%, N: 7.66%.

N,N-di[2-(3-propargyloxycinnamoyloxy)ethyl]-4-(4'-nitrophenylazo)aniline (2): 3-Propargyloxycinnamic acid (15.0 g, 74.2 mmole) and thionyl chloride (22 ml) were reacted in dichloromethane (80 ml) by refluxing for 6 h. After evaporation of the solvent and the excess thionyl chloride, the residue was recrystallized from *n*-hexane, affording 13.1 g (59.4 mmole) of 3-Propargyloxycinnamoyl chloride (Yield 80%). To a solution of the resulting chloride (13.1 g, 59.4 mmole) in dichloromethane (100 ml) was added triethylamine (7 ml) and *N,N*-di(2-hydroxyethyl)-4-(4'-nitrophenylazo)aniline (6.5 g, 19.8 mmole), and the solution was refluxed for 6 h. Then, methanol was added to the solution, and the solvent was evaporated. The residue was washed with water and recrystallized from butanol to afford 13.3 g (19.0 mmole) of *N,N*-di[2-(3-propargyloxycinnamoyloxy)-ethyl]-4-(4'-nitrophenylazo)aniline (Yield 96%). mp 140–141°C. IR (KBr) cm^{-1}: 3289 (H-C≡), 1710 (C=O) cm^{-1}. Elemental Analysis: Calcd. for $C_{40}H_{34}N_4O_8$ C: 68.76%, H: 4.87%, N: 8.02%, Found: C: 68.23%, H: 5.32%, N: 7.84%.

Polymerization

Polymerization and copolymerization of these bisacetylenic monomers were carried out by oxidative coupling. A typical polymerization procedure (for the case with monomer ratio of ***1*** to ***2*** = 8:2) is as follows: To a solution of ***1*** (1.6 g, 2.29 mmole) and ***2*** (0.4 g, 0.572 mmole) in N-methylpyrrolidinone (NMP) (10 ml) was added a few drops of *N,N,N',N'*-tetramethylethylenediamine and a catalytic amount of copper(I) chloride. The reaction mixture was stirred under a stream of oxygen at room temperature for 6 h. Then, the solution was diluted and poured into methanol. The precipitate was collected by filtration and washed with methanol and dried in vacuum. The polymer yield was quantitative. It should be noted that the methanol in which polymer solutions were poured, was slightly red when the polymers were precipitated, indicating that the polymerization was completed and no appreciable monomer remained. Because the polymerization yield was 100%, the copolymer composition was assumed to be the same as the monomer ratios. The general structure of these polymers is shown below:



Structure of polymers

Characterization.

Elemental analysis was performed by Desert Analytics, Tucson, Arizona. Differential Scanning Calorimetry (DSC) was carried out using a TA Instrument Calorimeter Model 910. FT-IR spectra were taken using a Nicolet 510p spectrophotometer. NMR spectra of polymers were taken in d-DMF using a Bruker Avance 400 (400 MHz) NMR spectrometer. Inherent viscosity was determined in NMP at 25°C. The visible spectra were taken using a UNICAM UV 300 spectrometer. The films were prepared on quartz panes by spin-coating from DMF solutions using a spin-coater with a heating device.

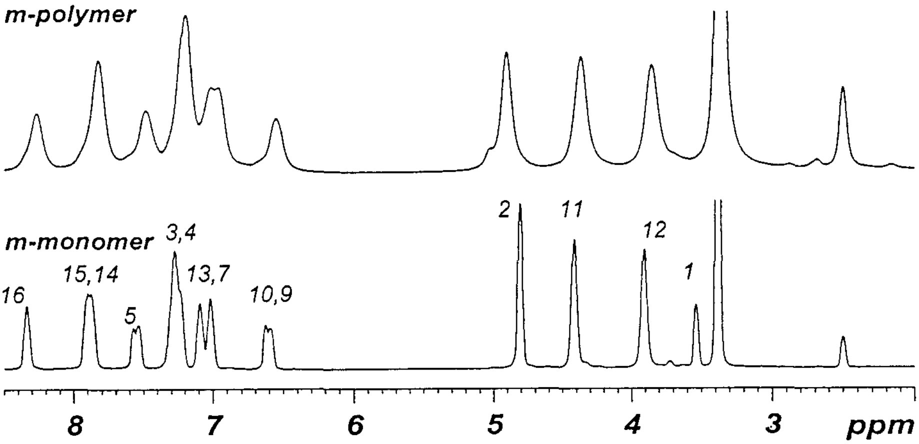
UV irradiation

The polymer films were irradiated on a hot stage with a 450W medium pressure mercury lamp of Ace Glass Inc, at a distance of 20 cm in air. The spectral characteristic in watts of the lamp is shown below:

Far U.V. 220-280 nm	Middle U.V. 280-320 nm	Near U.V. 320-400 nm	Visible 400-600 nm	Infrared 1000-1400 nm	Total radiated Energy
27.0	28.7	28.0	75.7	16.4	175.8

Results and discussion.

Fig. 2 shows ^{1}H NMR spectra of the monomers and polymers. The peaks due to terminal acetylenic protons (peaks 1) completely disappeared after polymerization. The peaks at 2.5 and 3.35 ppm are from the solvent *d*-DMSO (methyl protons and absorbed water, respectively).



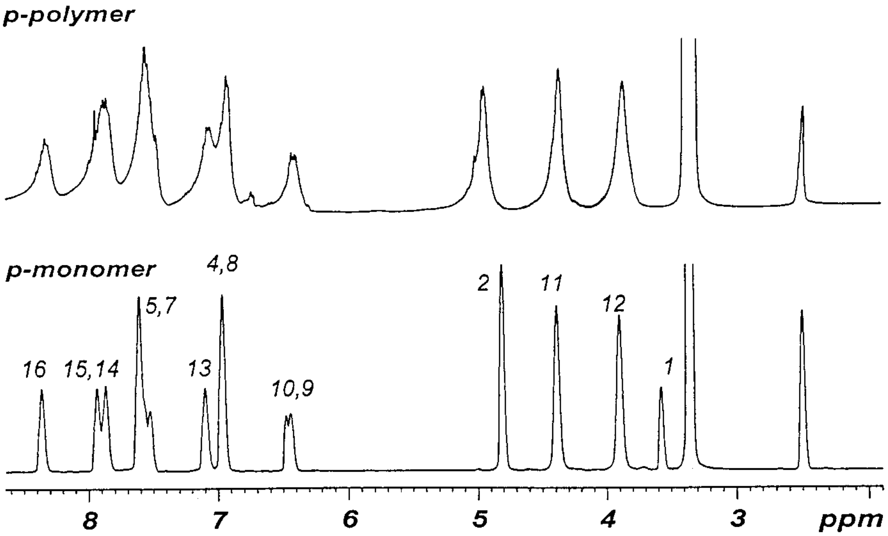


Fig. 2. ^{1}H NMR Spectra of *meta-* and *para*-poly(cinnamates) containing Disperse Red 19 chromophore, taken in *d*-DMSO. See the structure for peak numbers.

The FT-IR spectra of polymers no longer showed the peak at 3263-3289 cm^{-1} due to the terminal acetylenic proton, indicating the polymerization took place. All of the polymers were amorphous and soluble in DMF. However, the *para*-homopolymer precipitated in its DMF solution when left for several hours at room temperature, probably due to crystallization, and the precipitate was no longer soluble in DMF even on heating. The crystallized polymer was filtered and dried, and its DSC showed an endotherm peak at 150°C due to melting. However, the crystalline polymer was soluble in NMP, and reprecipitation with methanol gave again the DMF-soluble polymer. Therefore, its films were prepared immediately after dissolving in DMF. The film did not crystallize on standing. The 100% *meta*-polymer was also crystallizable. When its solution in DMF was kept for several days, the solution gradually became cloudy forming powdery precipitates. The precipitates were soluble in NMP. The polymers had inherent viscosity, η_{inh} of 0.2 - 0.5 dl/g in NMP at 25°C: The values of η_{inh} were as follows: 100%-*para*: 0.46, 80-*para*/20-*meta*: 0.48, 60-*para*/40-*meta*: 0.42, 40-*para*/60-*meta*: 0.59, 20-*para*/80-*meta*: 0.23, 100-*meta*: 0.26. The polymers gave films with excellent optical quality on spin coating from their DMF solutions at 45-50°C, when the inherent viscosity is greater than about 0.2.

Fig. 3 shows DSC curves of the 6 polymers. The exotherm due to the thermal cross-linking of diacetylenic groups starts at around 150°C, but this temperature is too high for maintaining the orientation of poled chromophore. Therefore, the thermal cross-linking is not suitable for cross-linking the poled polymers. The peaks above around 250°C (not shown in the figure) are due to thermal decomposition.

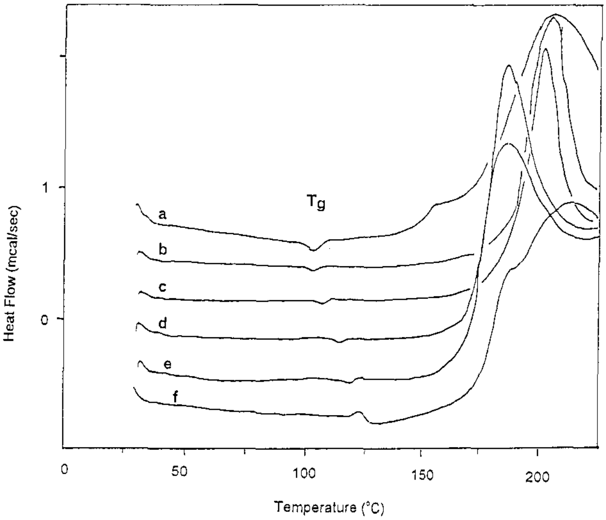


Fig. 3. DSC curves of poly(cinnamates): **a**: 100% *meta*. **b**: 20 *para*/ 80 *meta*. **c**: 40 *para*/60 *meta*, **d**: 60 *para*/40 *meta*. **e**: 80 *para*/20 *meta*. **f**: 100 *para*. Heating rate: 10°C/min.

Fig. 4 shows the visible absorption spectra of spin coated polymer film. The absorption is that of Disperse Red 19 dye and therefore the six polymers gave the same spectra. In order to see the magnitude of the *trans* to *cis* transformation by UV irradiation, spin coated films were irradiated first at room temperature. It is obvious that the *trans-cis* transformation takes place. However, in the case of irradiation at 110°C around T_g at which poling is carried out, the peak height decreased somewhat for the first 10 minutes. However, further 10 minutes irradiation the absorption intensity increased, and remained constant for 30 minutes irradiation. In the Dalton's work, the intensity decreased drastically with increase in the irradiation time. Although the irradiation source and conditions may be different, it seems that the high temperature (110°C) favors the *cis* to *trans* transformation, and equilibrium might have been established. After the irradiation at 110°C for 30 minutes, the film became completely insoluble in the solvents. It is possible that the cross-linking took place by the 2+2 photo-cycloaddition of the cinnamate group. However, the diacetylene groups are highly sensitive to UV irradiation, and although the diacetylene groups of these polymers are not topochemically polymerizable ones, they cause rapid cross-linking by radical coupling. The poly(benzoates) which do not have a C=C bond for cycloaddition, undergo rapid cross-linking with their diacetylene groups when irradiated with UV light at temperatures around 100°C (4). The irradiation at room temperature does not cause cross-linking appreciably, and therefore, it is necessary to irradiate at temperatures around Tg. The irradiated films were soaked in DMF for an hour, but the films did not swell nor peeled off from the quartz substrate.

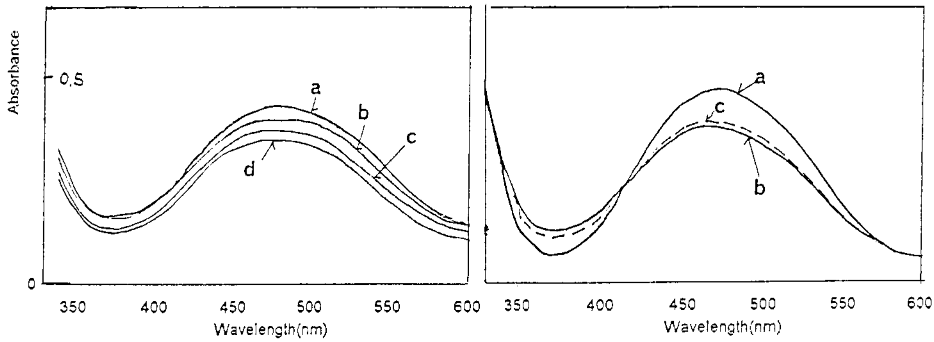


Fig. 4. Visible spectra of spin-coated films of copolymer (*para/meta* = 6/4) irradiated with UV light at room temperature (left: film thickness: 0.3 μm. **a**: 0, **b**: 10, **c**: 20, **d**: 30 minutes irradiation) and at 110°C (right: thickness: 0.2 μm, **a**: 0, **b**: 10, **c**: 20 and 30 minutes irradiation).

The 2-NLO coefficients of some of these polymers were determined at room temperature using a Q-switched Nd:YAG laser (1064 nm, 8 n, 10Hz). The *para*-polymer showed a d_{33} value of 250 pm/V while the *meta*-polymer had a much less value of 54 pm/V (6). This difference in the 2-NLO coefficients between the *para*- and *meta*-polymers is the same as the difference between the *para*- and *meta*-benzoates, indicating that the *para*-main chains are the choice for obtaining high SHG polymers. These 2-NLO coefficients given above are of the uncross-linked films. The detailed study on the 2-NLO properties will be reported in future.

Acknowledgements.

This work was financially supported by CONACYT (Consejo Nacional de Ciencia y Tecnología) under the contract No. 25259-A y 33001-U, and DGAPA (Dirección General de Asuntos del Personal Académico) of our university, under the contract number IN102401. The authors wish to thank Miguel A. Canseco for his technical assistance in DSC, and Gerardo Cedillo for NMR spectroscopy. The NLO coefficients were determined by Dr. Toshiyuki Watanabe of Tokyo University of Agriculture and Technology.

References

(1). Messier J, Kajzar F, Prasad P, Ulrich D, edits, *Nonlinear Optical Effects in Organic Polymers,* Kluwer Academic Publications, Dordrecht (1989)

(2). H.S.Nalwa H S, Miyata S, Edts. "Nonlinear Optics of Organic Molecules and Polymers." CRC Press, Inc. Boca Raton, FL, (1977)

(3). Miyata S, Sasabe H, edts. "Poled Polymers and Their Applications to SHG and EO Devices," Gordon and Breach Sci. Publishers, Amsterdam, (1977)

(4). Hernandez S, Beristain M F, Ogawa T, (2002) *Designed Monomers and Polymers,*5, No.1, 124-139.

(5). Hernandez S, Ogawa T, Watanabe T, Miyata S, (2002) *Mol.Cryst. Liq.Cryst.* 374, 503-512.

(6). Hernández S, Beristain M.F, Ogawa T, Watanabe T, Miyata S. *Macromol.Symp.* in press.

(7). M.Chen, L.Yu, L.R.Dalton, Y.Shi, and W.H.Steiner, (1991) *Macromolecules*, 24, 5421-5428.