perconducting properties; this implies that the Cu(1) layers in this structure play little role in superconductivity.

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Third-Order Susceptibilities of Soluble Polymers Derived from the Ring-Opening Metathesis Copolymerization of Cyclooctatetraene and 1,5-Cyclooctadiene

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There is currently a substantial research effort devoted to the development of new organic materials with large cubic optical nonlinearities and to gaining insight into the fundamental factors that lead to large optical nonlinearities.[1-3] Recent experimental[4-6] and theoretical[7-9] studies indicate that extended conjugation leads to large cubic susceptibilities. It would be desirable to develop general methodologies[10-12] for the synthesis of new materials that combine the electronic properties arising from extended conjugation and the processability advantages generally associated with polymers. Ring-opening metathesis polymerization represents a promising new route to materials with large third-order optical nonlinearities since inherent in the mechanism of the reaction is the *preservation of the degree of unsaturation present in the monomer*. This is in contrast to many radical, cationic, anionic, and Ziegler–Natta polymerizations in which an olefinic monomer will usually lead to a polymer with a fully saturated backbone.

We wish to report some preliminary results on the nonlinear optical properties of a new class of polymers synthesized by the ring-opening metathesis polymerization of highly unsaturated monomers. Mixtures of cyclooctatetraene, **1**, and 1,5-cyclooctadiene, **2**, have been polymerized by using the tungsten carbene complex **3** as the catalyst[13] (see Figure 1). The solution polymerization of monomers **1** and **2** in tetrahydrofuran leads to an essentially random copolymer.[14] The monomers contain exclusively cis double bonds and no attempt has been made to isomerize the double bonds in the resulting polymer. The general constitution of the copolymers is also shown in Figure 1 (an all-trans geometrical configuration is shown for simplicity).

The polymerizations of mixtures of **1** and **2**, where the mole fraction of **1** was varied from 0.10 to 0.50, were typically performed as described in the following procedure. The monomer mixture (100 μL, ~0.85 mmol) in 400 μL of a tetrahydrofuran solution containing 8.0 mg (0.01 mmol) of **3** was allowed to react for 6 h. Then 1200 μL of a tetrahydrofuran solution containing 36 mg (0.42 mmol) of $(CH_3)_3CC(O)H$, which destroys the catalyst,[13] and 24 μL (0.17 mmol) of mesitylene, an internal standard for gas chromatographic studies (vide infra), was added. After quenching, examination of the reaction mixture by gas chromatography allowed us to determine the number of moles of cyclooctatetraene and 1,5-cyclooctadiene incorporated into the polymer.[15]

The optical spectra of the copolymer solutions (an example of which is shown in Figure 2) provide insight into the conjugation lengths present. On the basis of previous studies of polyenes[16] and conjugated polymers[17] we would assign the bands at 316, 332, and 344 nm to segments of the polymer with 5 conjugated double bonds, bands at 384, 404, and 432 nm to segments of the polymer with 9 conjugated double bonds, and bands at 432, 464, and 496 nm to segments of the polymer with 13 conjugated double bonds. The segments with 5, 9, and 13 double bonds arise from incorporation of one, two, or three consecutive cyclooctatetraene monomers, respectively, into the polymer. In the copolymers that we have examined the distribution of conjugation lengths is dominated by the 5 double-bond segments with a significant amount of 9 double-bond segments, but there are quite few segments with 13 or more double bonds. From the variation of the solution spectra with monomer composition we can say that there is an *increase in both the percentage of olefinic carbons and the average conjugation length in the polymer as the percentage of cyclooctatetraene in the monomer mixture increases* as was seen in the previously reported copolymer films.[14]

Nonlinear optical properties of the polymer mixtures were studied as a function of the composition. The third-order susceptibilities of the copolymer solutions were determined by using wedged-cell third-harmonic generation (THG) techniques.[18,19] The 1.907-μm Raman shifted (H_2 gas) output from a Q-switched Nd:YAG laser was used

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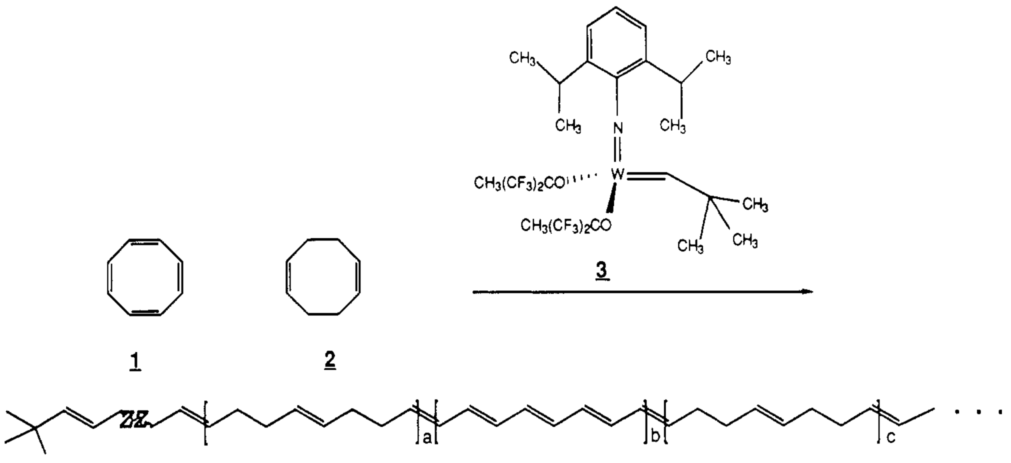

Figure 1. Synthesis of cyclooctatetraene/1,5-cyclooctadiene copolymers.

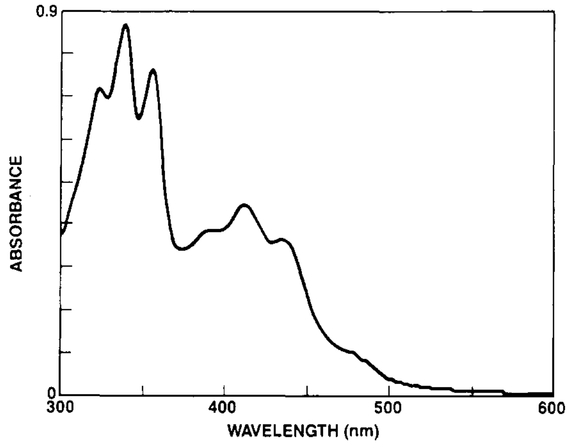

Figure 2. UV-visible spectrum of copolymer solution derived from 50% cyclooctatetraene, 50% 1,5-cyclooctadiene monomer mixture.

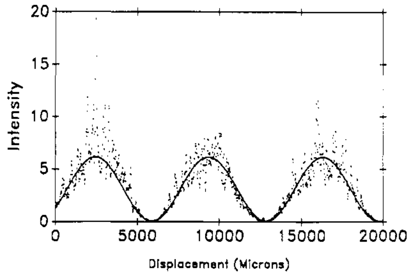

Figure 3. THG fringes of a solution of copolymer derived from 50% cyclooctatetraene, 50% 1,5-cyclooctadiene monomer mixture.

as the fundamental for THG measurements. Wedge THG interference fringes were observed by translating the cell normal to the laser beam. For the polymer solutions studied, simple fringing behavior was observed as shown in Figure 3.

The THG fringes were fit to the following expression:[19]

$$I(3\omega) = A \sin^2 (Bx) \qquad (1)$$

where $B = \pi/l_c \tan (\theta/2)$, x is the distance translated, and θ is the cell wedge angle, to obtain the amplitude A and the coherence length, l_c, for a solution. Measurements were also made by using toluene as a reference liquid in the same cell for a relative $\chi^{(3)}$ determination. $\chi^{(3)}$ for a given solution was calculated by using a simplified expression:

$$\chi^{(3)} = l_c^{-1}[(1 - R^{1/2})(\chi^{(3)}l_c)_g + R^{1/2}(\chi^{(3)}l_c)_r] \qquad (2)$$

where $R = A/A_r$ and the subscripts g and r refer to the window and the reference liquid, respectively.

Table I. Summary of Composition and Third-Order Optical Nonlinearities of Cyclooctatetraene and 1,5-Cyclooctadiene Copolymers

initial x_1	x_1 in polymer	1 in polymer, mmol	$\chi^{(3)}_p$,[a,b] 10^{-14} esu	γ_p,[a] 10^{-36} esu	γ'_p,[a] 10^{-36} esu
0.10	0.08	0.064	33	20	210
0.20	0.15	0.108	60	36	220
0.40	0.27	0.159	130	81	280
0.50	0.32	0.166	160	100	300

[a] Nominal uncertainty ±25%; relative values are more precise. [b] We have independently measured the $\chi^{(3)}$ of cyclooctatetraene, 1,5-cyclooctadiene, and $(CH_3)_3CC(O)H$ and have determined that correcting for their residual contributions alters the solution $\chi^{(3)}$ values by only 1–2%.

The $\chi^{(3)}$ of a copolymer solution contains the ensemble-average contribution from all components of the solution as indicated by the sum

$$\chi^{(3)} = \sum N_i l(3\omega) l^3(\omega) \langle \gamma_i \rangle \qquad (3)$$

where N is the number density, l is the local field factor, and $\langle \gamma \rangle$ is the hyperpolarizability. Since we have determined the amounts of monomers incorporated into polymer by gas chromatographic analysis, we know the total number density and mole fraction of the monomers in polymer in solution. Hence, we can calculate the average hyperpolarizability per monomer unit in polymer, γ_p, for the various compositions. We can also estimate the susceptibility corresponding to the neat copolymers using the following expression which is valid for dilute solutions:

$$\chi^{(3)}_p = [(\chi^{(3)}_{obsd} - \chi^{(3)}_s)/x_m + \chi^{(3)}_s]N^0_m/N^0_s \qquad (4)$$

where x_m is the solution mole fraction of monomer converted to polymer, $\chi^{(3)}_s$ is the pure solvent susceptibility, and N^0_m and N^0_s are the neat monomer and solvent number densities, respectively. This estimation assumes that the monomer goes to polymer at roughly constant density. It should be emphasized that the $\chi^{(3)}$ calculated in this way corresponds to the neat polymer with the local field factor of the solution.

Table I summarizes the results of the THG studies along with results on the polymer composition determined from gas chromatographic analysis. The gas chromatographic results show that the mole fraction of the cyclooctatetraene in the polymer differs from the mole fraction in the monomer mixture. There is less cyclooctatetraene incorporated into the polymer than one would expect on the basis of the monomer composition, indicating that 1,5-cyclooctadiene reacts faster than cyclooctatetraene. Also, the total percent conversion decreases as the initial cyclooctatetraene fraction is increased. The γ_p and $\chi^{(3)}_p$ values listed in Table I are based on the total mole fraction of monomer incorporated into polymer.

The $\chi^{(3)}$ and γ_p values of the copolymers increase substantially with increasing fraction of **1**. This reflects both the increasing concentration of conjugated units and the increasing conjugation length with higher fraction of **1**. It is expected that the nonlinearity of the units of **2** in the polymer is negligible compared to the units of **1**, assuming so one can calculate the hyperpolarizability per unit of **1** in the polymer, γ'_p, as listed in Table I. The fact that γ'_p increases with increasing fraction of **1** in the polymer shows that the presence of the increased conjugation lengths (nine double-bond segments) results in enhanced nonlinearity. The value of γ'_p for the copolymer dilute in **1**, in which the units of **1** are mostly isolated, is somewhat lower than but compares favorably to the hyperpolarizability measured[20] for a four double-bond polyene for which $\gamma = 400 \times 10^{-36}$ esu. It is of interest to note that the value of γ we determined for **1** from measurements of the neat liquid is much lower, $\gamma = 5 \times 10^{-36}$ esu, probably due to poor p-orbital overlap.

The magnitude of $\chi^{(3)}$ of the copolymer with 32% cyclooctatetraene is $\sim 2 \times 10^{-12}$ esu. By comparison a solution measurement on β-carotene (with 11 conjugated double bonds) gave a value of $\chi^{(3)} = 9 \times 10^{-11}$ esu, which is in agreement with a recent measurement.[20] Measurements on neat polyacetylene have given a value of 1.3×10^{-9} esu (enhanced by three-photon resonance) at 1.9 μm.[6] While the $\chi^{(3)}$ of the copolymer is modest, this work demonstrates that the ring-opening metathesis polymerization methodology can be used to produce materials with substantial nonlinearities and is flexible enough to allow tailoring of materials properties. It should be noted that transparent uniform films of the soluble polymers can readily be prepared by spin coating. Since functionalized cyclooctatetraene derivatives can be polymerized in a manner[14] similar to that described here, a wide range of polymers with various pendant groups can be prepared. Processability is an important issue for applications of such materials in nonlinear optical devices such as nonlinear wave guides.[21] Additionally, scattering losses in the polymer films must be minimized. By use of the ring-opening metathesis polymerization methodology it may be possible to develop soluble, processable materials with low scattering losses and high nonlinearities. Such routes are currently under investigation.

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