film on a glass substrate for several seconds. Figure 3a shows a series of embedded "conducting lines" of approximately 0.5 mm thickness in insulating BBB films treated in this way. The conductivity of these lines is approximately 50 S/cm. The conductivity of the shiny-brown polymer background remains unaffected by the laser heating. Using this masking technique, we can produce conducting lines approximately 10 µm in width (width is determined by the slit, laser focusing and exposure time). The pattern shown in Fig. 3a is stable in air and upon subsequent heating to 200 °C. We assume that laser annealing affects the polymer mainly through heating, so the "conducting lines" are composed of cross-linked polymers with the properties described above. Upon exposure to fluorine, the "conducting lines" remain unaffected, but the remaining pristine BBB becomes completely transparent and colorless. Figure 3b pictures this new structure consisting of "conducting lines" in a transparent material. This structure is stable in a humidity-free environment.

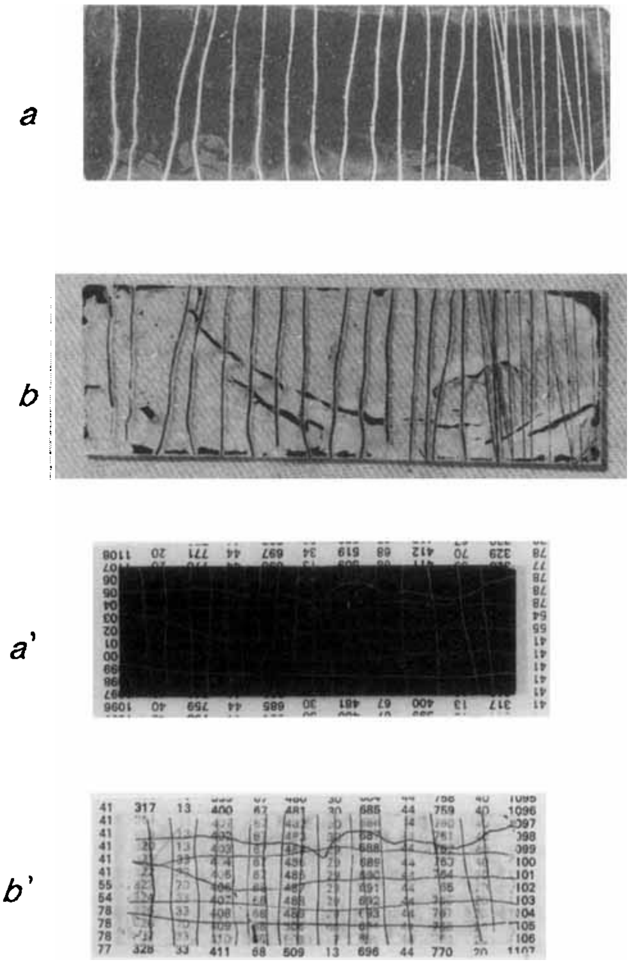

Fig. 3. a) "Conducting Lines" produced by the laser annealing technique in BBB polymer. The conducting lines are shiny-silver and reflect light and thus appear more bright in photo. a') Fine conducting lines produced by laser annealing of BBB. b) After fluorination: The "conducting lines" in a transparent film. b') Same as a', but after fluorination. (Numbers in background shown to emphasize degree of transparency).

We have now preliminary evidence that the heating and fluorination process affects other rigid-rod polymers as well. The transparent films so produced are optically anisotropic and less affected by humidity. The fluorination of polyacetylene was published recently[9] but in this case the fluorinated material is white rather than transparent.

The possibility to produce highly aligned transparent films with anisotropic optical properties and particularly the generation of spatially selective conductive patterns in insulating aligned transparent polymers opens new routes for applications in fields such as lithography, microelectronics, optics and molecular electronics. For instance, "writing" using selective laser heating and eliminating the rest of the film by fluorination and washing (using water or other solvents) might be important in both lithography and microelectronics. The fabrication of very fine grids composed of fine alternate stripes of conducting and transparent polymers with anisotropic optical properties is another interesting possibility. Optical disks should be considered as well. Generally speaking, the possibility to fabricate miniature conducting microstructures with novel electronic properties is now more realistic.

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Highly Conjugated, Substituted Polyacetylenes via the Ring-Opening Metathesis Polymerization of Substituted Cyclooctatetraenes**

By *Christopher B. Gorman*, *Eric J. Ginsburg*, *Seth R. Marder*, and *Robert H. Grubbs**

Soluble, highly conjugated polymers such as substituted polythiophenes, poly(*p*-phenylene vinylenes),[1] and most

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recently polyalkylanilines,[2] have had a large impact on the study of conductive polymers. Soluble polymers can be more fully characterized and more easily processed. Despite intensive study and synthetic effort, there are few tractable or soluble conjugated derivatives of polyacetylene.[3,4] Substitution of polyacetylene via the polymerization of substituted acetylenes results in materials with low effective conjugation lengths, as evidenced by their high-energy visible absorption spectra and comparatively low iodine-doped conductivities.[5] This low conjugation length is presumably due to twisting around the single bonds in polyacetylene resulting from steric repulsions of the side groups[6,7] (Fig. 1).

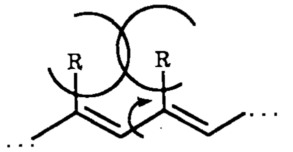

Fig. 1. Chain twisting in substituted polyacetylene.

Recently, *Klavetter* and *Grubbs* reported the synthesis of polyacetylene by the ring-opening metathesis polymerization[8] (ROMP) of cyclooctatetraene (COT).[9,10] Here we report the ROMP of substituted cyclooctatetraenes: a route to a variety of highly conjugated, partially alkyl-substituted polyacetylenes. These polymers have a substituent on the average every eight carbons, rendering some of them partially soluble. Polymerization can be accomplished in a few minutes in a nitrogen drybox, resulting in free-standing films which are generally gold, shiny, and flexible.[11]

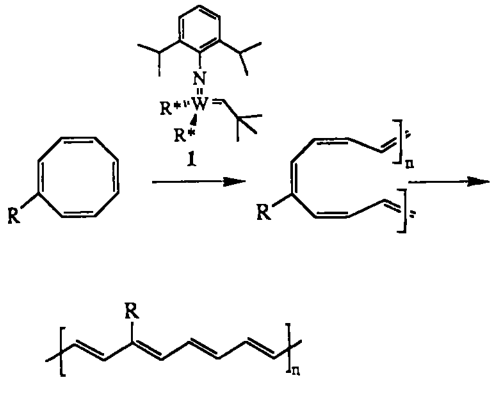

Fig. 2. Polymerization of Cycloocatatetraene Derivatives. R* = $(CF_3)_2(CH_3)CO$; R = Me, *n*Bu, octyl, octadecyl, Ph, *t*Bu, neopentyl.

These films can be iodine doped to a conductive state (Table 1). Moreover, in contrast to poly-cyclooctatetraene (polyacetylene) which shows large optical scattering losses due to its crystallinity, the alkylCOT polymers are amorphous and show low scattering losses.[12,13]

Table 1. Conductivity and spectroscopic data.

polymer	σ (S/cm)	y [a]	abs. max. initially [b]	abs. max. T ≈ 6–12 hrs. [b]
Poly-MethylCOT	15–44	–	522 [c]	–
Poly-*n*-ButylCOT	0.25–0.7	0.10 0.13	462	614
Poly-OctylCOT	15–50	0.11–0.19	480	632
Poly-OctadecylCOT	0.60–3.65	0.14–0.16	538	630
Poly-PhenylCOT	0.3–0.6	0.19–0.28	522	620
Poly-*t*-ButylCOT	$<10^{-8}$	≈0.03	302	432
Poly-NeopentylCOT	0.2–1.5	0.11–0.18	412, 628	634
Poly-NeopentylCOT after recasting solution:	15–21	0.13–0.17	–	–

[a] Based on the molecular formula $(C[H/R]I_y)_x$. [b] Spectra taken in tetrahydrofuran. Wavelength in nm. [c] Very small amount of material that leached out of the film.

Whereas poly-methylCOT, like polyacetylene, is somewhat brittle and completely insoluble, films of poly-RCOT with straight chain alkyl substituents of at least four carbons are flexible and partially soluble in solvents such as tetrahydrofuran (THF) and dichloromethane. When a film of poly-*n*-butyl-, poly-octyl- or poly-octadecylCOT was stirred with THF, a red/brown solution resulted that contained 1–2 mg/mL of polymer, and which turned blue upon standing overnight. Solutions stored under argon at −50 °C in the dark did not turn blue. We propose that the color change is due to an increased electron delocalization arising from the *cis* double bonds in the nascent polymer isomerizing to give a material with predominantly *trans* double bonds, although aggregation phenomena cannot be ruled out at this time.[14] Similar changes have been observed in the optical spectra of films of polyacetylene,[15] and the related poly-trimethylsilylCOT.[16] Also, red-shifts in the absorption spectra of short polyenes upon *cis-trans* isomerization have been observed by *Schrock* and coworkers.[17] If not diluted at least tenfold before isomerization, 1–2 mg/mL solutions of the *cis* polymer gelled or precipitated. The predominantly *cis* isomer of these polymers is soluble whereas the *trans* isomer is much less so. This observation is consistent with previous observations on oligomeric polyenes.

Nascent poly-neopentylCOT was completely soluble, but also precipitated upon isomerization to the *trans* form if not diluted. Blue suspensions that resulted from the isomerization of concentrated solutions, however, were recast into gold films that displayed iodine-doped conductivities two orders of magnitude higher than the original material. The aromatic side-chain derivative poly-phenylCOT was about as soluble as poly-*n*-butylCOT in the *cis* form, but was almost completely insoluble in the *trans* form. Poly-*t*-butylCOT was freely soluble but was yellow-orange in color, indicating a low effective conjugation length. Thus, modifications to the polymer backbone which increase its solubility seem to reduce its conjugation length.

Gel permeation chromatography on solutions of the "*cis*" polymers indicated that the solutions contained high molecular weight materials (Table 2) although molecular weight distributions were very broad in several cases. The retention times of the polymers generally increased after isomerization, suggesting an increase in hydrodynamic radius.

Table 2. Molecular weights.

polymer	M_n	M_w
Poly-*n*-ButylCOT	33200	153400
Poly-OctylCOT	35900	369000
Poly-*t*-ButylCOT	58300	71900
Poly-NeopentylCOT	23400	27100
Poly-PhenylCOT	30600	121100

The polymers were examined by ^{1}H NMR and Raman spectroscopy. The NMR spectra of all the polymers showed broad multiplets between 6 and 7 ppm and broad signals in the regions expected for the side groups, indicative of a polymeric, olefinic chain. Raman spectroscopy provided further evidence of a conjugated chain. Two peaks, assigned as the A_g C-C stretch (ν_1) and A_g C=C stretch (ν_2) in *trans*-polyacetylene were observed in all the spectra (Table 3), except for that of poly-phenylCOT, which displayed a complicated spectrum dominated by phenyl stretches. No peaks were seen that corresponded to the *cis* form of polyacetylene, probably since no precautions were taken to prevent isomerisation caused by the 488 nm laser light. In unsubstituted polyacetylene the infrared C-H stretching vibrations at 740 cm^{-1} and 1015 cm^{-1} are diagnostic for *cis* and *trans* material, respectively. The infrared spectra of the substituted polyacetylenes are not as useful, since the vibrations of the side chains obscured those of the main chain.

Table 3. Raman stretching vibrations of polyacetylene derivatives (cm^{-1}).

polymer	ν_1	ν_2
Polyacetylene[18]	1090–1120	1470
Poly-MethylCOT	1126–1132	1516
Poly-*n*-ButylCOT	1132	1514
Poly-OctylCOT	1114–1128	1485
Poly-*t*-ButylCOT	1147	1539–1547
Poly-NeopentylCOT	1131	1509

Several attempts have been made to correlate the effective conjugation length of a polyene with its absorbance maximum. Based on the extrapolation of polyene absorption data obtained from a variety of workers[19, 20] to the band gap of polyacetylene,[21] the *trans* form of these polymers have an effective conjugation length of at least 25 double bonds. Lower energy absorption maxima are seen in the solid state. A thin film of poly-octylCOT has a broad absorption centered around 650 nm which is comparable to that observed for a thin film of native polyacetylene.[21]

In summary, ROMP of alkyl-substituted cyclooctatetraenes produces polyacetylene derivatives in which the substituents are placed at a sufficient distance apart to allow conjugation along the backbone of the polymer and still provide for solubility in the *cis* configuration. Work is underway using the RCOT/ROMP methodology to develop other polyacetylene derivatives which are more soluble, more conductive, and air-stable.

Experimental

Polymerization was effected by adding 50–150 equivalents of the liquid monomer to 1–2 mg of the tungsten alkylidene catalyst [22] dissolved in a minimum (200 µL) of pentane and 1–2 µL of THF. After the yellow solution began to turn orange/brown, it was transferred by pipette onto a glass plate and allowed to harden into a film over the course of an hour or so. Films were peeled from the plate and used for conductivity measurements. Doping was accomplished by exposing the films to iodine vapor for 3 to 6 hours in a previously evacuated chamber followed by pumping (<0.01 torr) for approximately one hour to remove excess iodine. Films exposed to iodine immediately became blue-black in color and remained flexible. Conductivities were measured using a four-point probe in a nitrogen drybox or a four-wire probe attached to a Schlenk line. [23] Similar conductivities were seen using both methods.

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Research News

Monolayers and Langmuir–Blodgett Multilayers of Discotic Liquid Crystals?

By André Laschewsky*

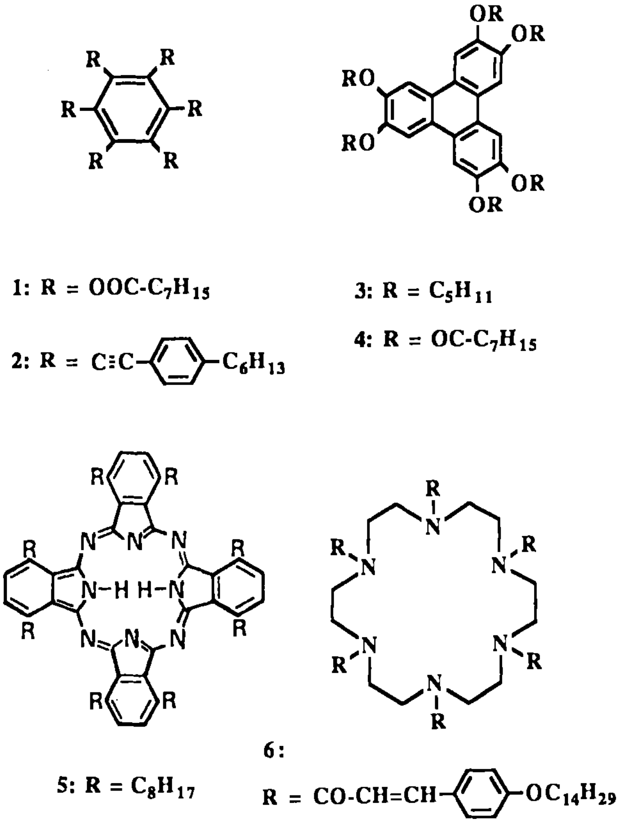
1. Discotic Liquid Crystals

Discotic liquid crystals[1] were discovered in 1977. They are formed by disk-shaped molecules, i.e. typically by large planar aromatic, or by rather inflexible macrocyclic moieties, surrounded by a number of flexible so-called "wing groups". A selection of discotic liquid crystals (LCs) is shown in Figure 1.

Discotic LCs exhibit columnar mesophases which distinguish them from the well-known calamitic (rod-shaped) LCs. These columnar phases are characterized by stacks of the disk-shaped cores, packed in various ways.[1]

2. Monolayers and Langmuir–Blodgett Multilayers

Ordered monomolecular layers are formed by the self-organization of water-insoluble amphiphilic molecules at the gas-water interface.[3] The standard amphiphiles used for monolayers have a polar head group and one or two hydrophobic chains, e.g. fatty acids or phosphatidylcholines respectively. Under appropriate conditions, the monolayers of many amphiphiles can be transferred successively onto solid substrates, by dipping the substrate vertically or horizontally



1: R = $OOC\text{-}C_7H_{15}$

2: R = $C{\equiv}C\text{-}C_6H_4\text{-}C_6H_{13}$

3: R = C_5H_{11}

4: R = $OC\text{-}C_7H_{15}$

5: R = C_8H_{17}

6: R = $CO\text{-}CH{=}CH\text{-}C_6H_4\text{-}OC_{14}H_{29}$

Fig. 1. A selection of discotic liquid crystals [2, 9, 10].

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