Soluble, Highly Conjugated Polyenes via the Molybdenum-Catalyzed Copolymerization of Acetylene and Diethyl Dipropargylmalonate

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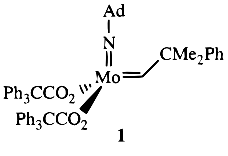
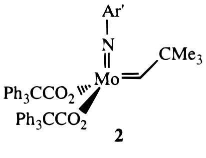
We recently reported[1] the cyclopolymerization of diethyl dipropargylmalonate[2−5] (DEDPM) by **1** and **2** to give soluble dark red polyenes that contain only six-membered rings as a consequence of a selective head-to-tail cyclopolymerization process (eq 1). The lowest energy λ_{max} (for the polymer made from 120 equiv of DEDPM) was found to be 534 nm. In order to increase the conjugation length (while hopefully maintaining solubility and relative air stability), we felt that it would be desirable to insert acetylene "spacers" between sterically demanding DEDPM units, i.e., to prepare random copolymers of DEDPM and acetylene. There is only one report of a controlled polymerization of acetylene by a well-defined catalyst,[6] as the rate of propagation is usually much greater than the rate of initiation. Synthesis of a copolymer from two monomers with homopolymerization reactivity differences as great as suspected between DEDPM and acetylene is an additional significant challenge.[7,8] We have found that it is possible to synthesize random copolymers of acetylene and DEDPM if the rate of addition of acetylene to **1** or **2** in the presence of DEDPM is tightly controlled.



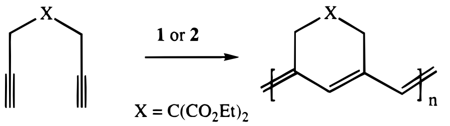
1

Ad = adamantyl



2

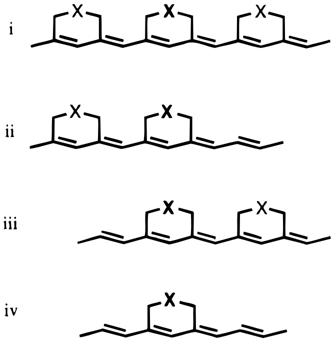
Ar' = 2-*t*-butylphenyl



(1)

Typically a solution of DEDPM in toluene was added to a solution of initiator **1** in toluene followed by addition of purified acetylene through a computer-controlled mass flow controller into the head space immediately above the stirring solution.[9] The acetylene was added in a linearly decreasing manner starting from a selected initial rate over a preset period of time.[10] The color of the reaction mixture changed from orange to red to purple, and in the cases where the polymer has a high acetylene content (>1 acetylene per DEDPM), to navy blue. The resulting polymers form intensely colored solutions, and upon evaporation of the solvent, films that have a copper-like luster. All such films can be redissolved readily in chloroform, THF, dichloromethane, and toluene; they are insoluble in pentane and ether. The yields of the copolymers ranged between 90 and 100%.

NMR methods are useful for characterizing the copolymers. The acetylene content in the polymer could be determined by proton NMR by integrating the olefinic resonances versus the methylene resonances in the ethyl groups or in the six-membered ring. As shown in Table 1 the degree of acetylene incorporation corresponds to the amount of acetylene added. A useful diagnostic resonance in ^{13}C NMR spectra is that due to the quaternary carbon atom in the six-membered ring.[1] The resonance for the homopolymer (i below; X = C(CO$_2$Et)$_2$; Figure 1a)[1] shows some fine structure that we ascribe to as yet undefined conformers. Three basic types of quaternary carbon resonances can be distinguished by ^{13}C NMR in the copolymers (Figure 1b−d). One is a quaternary carbon atom in a homopolymer triad (type i) at 54.5 ppm. A second is a quaternary carbon atom in a triad of type ii or iii at 54.2 or 54.1 ppm. A third is a quaternary carbon atom in a triad of type iv at 53.9 ppm. The ratio of triads ii and iii, which are inherently different as a consequence of the asymmetry of the six-membered ring, is approximately 1:1, as one would expect. The fact that all four resonances have about the same intensity in the "1:1 copolymer" (Figure 1c) is consistent with an essentially statistically random incorporation of acetylene and DEDPM, and the lack of any significant side reaction involving acetylene, such as trimerization. (The failure of **1** and **2** to function as catalysts for the ring-opening of norbornenes and substituted norbornadienes[1] suggests that "backbiting" into a polyene sequence formed by incorporation of several equivalents of acetylene would be unlikely in any case.) The quaternary carbon resonance characteristic of triad iv clearly increases with increasing acetylene content. The presence of more than one acetylene "spacer" between six-membered rings leads to further fine structure and overall broadening of the quaternary carbon resonances (Figure 1d). We propose that the quaternary carbon resonance is sensitive to pentad structure and that the broadening of the resonance in Figure 1d overall is the result.



UV/vis spectra reveal that λ_{max} and ϵ_{max} correlate smoothly with the amount of acetylene incorporated (Table 1). Incorporation of 1.5 equiv of acetylene per DEDPM yields a completely soluble, blue polymer with a λ_{max} value close to 600 nm, consistent with a very high degree of conjugation. Polymers containing more than 1.5 equiv of acetylene per equivalent of DEDPM were found to be increasingly insoluble in chloroform, THF, dichloromethane, or toluene.

The molecular weights and polydispersities of several 1:1 copolymers prepared by using **1** and **2** are listed in Table 2. The molecular weight was determined by GPC using a viscometry detector versus a polystyrene calibration curve. Although viscometry is not likely to provide reliable absolute molecular weights for polymers of this type,[11] relative molecular weights and polydispersities are useful. Some dependence of molecular weights and polydispersities on the type of initiator, the

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Table 1. Acetylene Incorporation Determined by ^{1}H NMR and UV/Vis Data for DEDPM/Acetylene Copolymers Using 1 as Initiator in Toluene.

entry^a	acetylene theory (%)^b	acetylene found (%)^c	λ_{max} (nm)^d	ϵ_{max} (cm^2/g)^d
1	50	53	548	47 300
2	75	81	562	55 200
3	100	101	576	81 000
4	100	96	576	69 700
5	120	119	586	75 700
6	120	121	584	76 600
7	150	153	598	86 300

[a] All runs with 20 mg (0.021 mmol) of **1**, 12 mL of toluene, and 30 equiv of DEDPM (0.63 mmol, 149 mg). [b] Mole percentage of acetylene relative to DEDPM. [c] Determined by ^{1}H NMR. [d] In CH_2Cl_2.

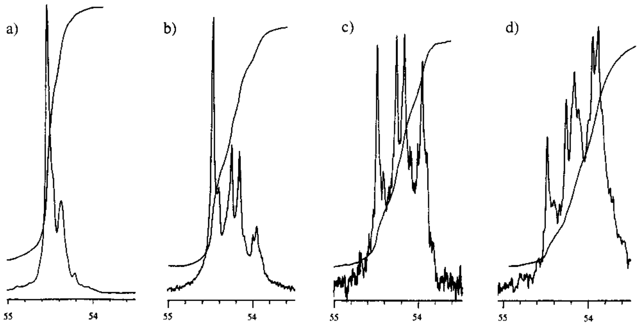

Figure 1. Quaternary carbon resonances of (a) homopolymer (DEDPM; see ref 1) and copolymers with different monomer compositions (DEDPM:acetylene): (b) 1:0.53; (c) 1:1.01; (d) 1:1.53.

Table 2. GPC Data for Acetylene/DEDPM Copolymers^a Prepared using 1 and 2 in Toluene as a Function of Concentration, Stirring Rate, and Acetylene Addition Mode

entry	initiator (μmol/mL)	stirring^b	t_{add} (min)^c	$(m/t)_0$ (mL/min)^d	M_n^{e}	M_w/M_n^{e}
1^f	**1** (1.75)	slow	10	3.12	91 000	5.7 (m)
2^g	**1** (1.75)	slow	4	7.70	34 000	1.97 (u)
3	**1** (1.40)	fast	4	6.20	8 900	1.69 (u)
4	**1** (0.93)	fast	3	8.27	15 000	1.54 (u)
5	**1** (1.58)	medium	3	6.20	69 000	1.75 (u)
6	**2** (1.69)	fast	4	7.55	4 800	1.78 (bi)
7	**2** (1.13)	fast	4	7.55	19 900	2.05 (bi)
8^h	**2** (1.13)	fast	3	6.67	6 700	1.46 (bi)
9	**2** (0.75)	fast	3	6.67	15 600	1.72 (u)^i
10	**2** (0.75)	fast	3	6.67	24 500	1.70 (u)^i
11^j	**2** (1.69)	medium	2	10.00	17 000	1.68 (u)

[a] 30 equiv of acetylene and DEDPM; 1 equiv of initiator. [b] Slow = small stirring bar, medium = large stirring bar with slow stirring, fast = vigorous stirring. [c] Acetylene addition time. [d] Initial mass flow. [e] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek); (u) = unimodal, (bi) = bimodal, (m) = multimodal distribution (PDI determined over entire peak area). [f] λ_{max} = 578 nm; ϵ_{max} = 75 200; acetylene found = 92%. [g] See entry 4 in Table 1. [h] 1 min delay of acetylene addition after addition of DEDPM. [i] Low molecular weight shoulder present. [j] 2 min delay.

concentration of initiator and DEDPM, and the rate of addition of acetylene can be observed, although the trends are not clear-cut. Unimodal distributions are observed more often with initiator **1** than with initiator **2**. Polydispersities are typically higher (1.4–2.0) than in the poly(DEDPM) homopolymer, most likely since the copolymerization is a complex process that could involve as many as eight chain propagation steps (two homopolymerization and two cross-polymerization rates for two different alkylidene rotamers[12]).

In the past copolymers that contain unsubstituted polyene sequences usually have been prepared by ring-opening of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (TCDT); poly(TCDT) sequences are then transformed into polyacetylene by heating.[13–16] The results reported here suggest that it is possible to employ acetylene itself as a comonomer. The disadvantage is that the polydispersity of such polymers is considerably larger than is typical for ring-opening metathesis polymerizations involving well-defined catalysts,[17] and the structure of the copolymer is not known with a high degree of certainty. In future studies we hope to determine whether initiators **1** and **2** are unique in their ability to control copolymerizations employing acetylene, and whether monomers other than DEDPM can be employed successfully.

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(9) The following is a typical polymerization procedure. A stock solution of **1** (2 mL, 0.0105 M) and 9 mL of toluene (distilled from sodium benzophenone ketyl and passed through dry alumina) were added to a reaction flask in a Vacuum Atmospheres dinitrogen-filled drybox. DEDPM (149 mg, 0.63 mmol in 1 mL of toluene) was added to the initiator. The system was sealed and acetylene (15.4 mL, 0.63 mmol) addition was begun within a few seconds. Acetylene was added with a linear decay over a period of 4 min with an initial mass flow of 7.7 mL/min. Within 30 s the reaction mixture turned deep red and after 2 min purple. After 6 h 16 μL of benzaldehyde was added and the solution was stirred for another hour. The solution was passed through alumina and all volatile components were removed in vacuo, leaving a dark purple film with a copper-like luster. All operations were carried out under dinitrogen and the polymers were exposed to air only briefly for GPC analysis and UV/vis measurements.
(10) The gas addition apparatus consisted of a MKS Instruments Inc. mass flow controller powered by a +15/−15 V power supply, a Macintosh II computer equipped with a National Instruments Lab-NB data aquisition board and Lab View (National Instruments) data aquisition software, a hydropurge moisture in-line trap and a hydrocarbon in-line trap (both Alltech Associates), and an all-metal addition system with valves and quick connects by Swagelock.
(11) We have shown by MALDI/TOF mass spectroscopy that the molecular weight of poly(DEDPM) homopolymers that contain six-membered rings is that expected on the basis of the number of monomers added, whereas the apparent molecular weight by viscometry is 2–2.5 times greater; unpublished results. We assume that roughly the same discrepancy exists for the polymers prepared here.
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