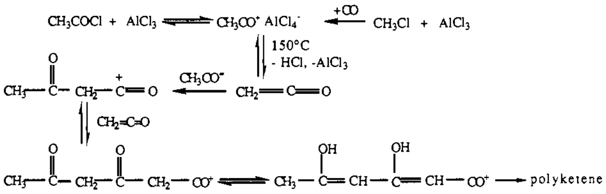
We suggest that the polymerization involves initial ionization of the acetyl chloride–aluminum trichloride complex to the acetyl cation followed by slow deprotonation at the reaction temperature to form ketene in situ. Ketene is then immediately acylated by acetyl cation or subsequently by the growing polymeric acyl ions.



The theoretical elemental composition for polyketene is C 57.1%, H 4.8%, and O 38.1%. We found an increase in the carbon content of the polymers with prolonged reaction time (after 2 h C, 62%, H, 4.5%, 20 h C, 64%, H, 4.3%, and 72 h C, 70%, H, 4.2%). These data suggest progressive dehydrative condensation and cross-linking of polyketene (poly(oxyacetylene)) during prolonged reaction, a process well-known for open chain oligo-β-carbonyl compounds.[13a] Aromatized phenolic rings can also be formed, similar to hydroxyaromatic ring formation from open chain poly-1,3-ones.[13b]

Interestingly, McElvain et al. in 1940[14] reported the formation of low molecular weight and insufficiently characterized polyketene by polymerizing ketene diethylacetal in the presence of cadmium chloride and subsequent hydrolysis. Wudl[15] has now succeeded, based on substantial improvement of McElvain's approach, in obtaining high molecular weight well-defined polyketene, which is similar to our polymer but of high purity and molecular weight. This indicates the more complex nature of the in situ polymerized system, which, however, can be directly obtained from inexpensive simple acyl halides.

Elemental analysis of the polyketenes obtained in the metal chloride catalyzed dehydrochlorinative polymerization always showed the presence of some chlorine (2–4%). With TGA and SEM/Edax measurements,[16] the decomposition profiles of the polymers show the loss of volatiles, and all samples showed the presence of inorganic residues. In samples of $AlCl_3$- and $TiCl_4$-catalyzed polymerization it was proven by SEM/Edax and FT-IR that the residue was aluminum trioxide and titanium dioxide, respectively. As it was not possible to remove all the metal chloride residues by acid wash, it seems that they are complexed very efficiently by the polymer, probably via 1,3-keto–enol complexation.

In addition to acetyl chloride, acetyl bromide (with $AlBr_3$), acetyl fluoride (with BF_3 catalyst and at more elevated (220 °C) temperature), and homologous substituted enolizable acetyl halides also undergo dehydrohalogenative polymerization. So far substituted polyketene was prepared from CH_3CH_2COCl, $(CH_3)_2CHCOCl$, $CH_3CH_2CH_2COCl$, $CH_3CH_2CH_2CH_2COCl$, $(CH_3)_3CCH_2COCl$, $(CH_3)_3SiCH_2COCl$ (giving both poly(trimethylsilylketene) and polyketene) as well as from phenylacetyl chloride ($C_6H_5CH_2COCl$) and some of its substituted derivatives. With substituent groups, particularly bulkier ones, elemental analyses of the polymers show much better agreement with theoretical values for linear polyketenes, indicating limited or no condensation and cross-linking. They also show improved solubility. For example, poly(phenylketene) is soluble in THF, and GPC analysis showed three major fractions of the polymer with average MW of 10^6, 10^5, and 10^4.

The reported new cationic dehydrohalogenative polymerization allows preparation of polyketenes from inexpensive and easily available acetyl halides and their derivatives, making them unexpected new monomers. Studies are underway to explore this interesting new class of polymers.

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[13] (a) Harris, T. M.; Harris, C. M. *Tetrahedron* **1977**, *33*, 2159. Gilbreath, S. G.; Harris, C. M.; Harris, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 6172.

[14] Johnson, P. R.; Barnes, H. M.; McElvain, S. M. *J. Am. Chem. Soc.* **1940**, *62*, 964.

[15] Khemani, K. C.; Wudl, F. accompanying communication.

[16] These measurements were carried out by Dr. E. Zadok in Israel.

Poly(ketene) (PKT)

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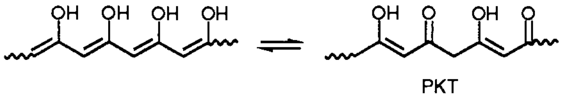
We report here the preparation and full characterization of poly(ketene) from a precursor polymer. Conjugated backbone polymers are of current interest due to their electronic and optical properties.[1] In the recent past it was discovered that ether substituents on the backbone of conjugated polymers cause a decrease in the semiconductor energy gap (Eg) of these organic conductors.[1] An unusual "conjugated backbone" polymer is poly(ketene) (PKT), a poly(hydroxyacetylene). The latter, also known as "poly(1,3-diketone)",[2b] was brought to our attention by Professor Olah[3] in connection with collaborative investigations of optical and electronic properties of a polymer prepared by his group.



PKT

Preparations of poly(ketene) have been claimed at various times in the past.[2,4–6] These involved hydrolysis of a precursor polymer,[2a] the oxidation of poly(vinyl alcohol),[4,6] and the action of a Lewis acid on ketene and diketene.[5] More recently, it was prepared by Lewis acid catalyzed polymerization of in situ generated ketene.[3] Of all the methods mentioned above, we opted for the hydrolysis of a poly(ketene dialkyl acetal)[7] because the deprotection step of ketals to ketones is known to be more efficient and milder than the oxidation of alcohols to ketones [e.g., poly(vinyl alcohol) → PKT]. Implicit is the requirement that ketene dialkyl acetal could efficiently be polymerized to a high molecular weight macromolecule.

Polymers of ketene diethyl acetal,[2a,b] mixed ketene acetals,[2b] and ketene dibutyl acetal[8] and a copolymer of ketene diethyl and ketene dibutyl acetal[8] were prepared by cationic polymerization, principally by using the procedure developed by McElvain.[2a] All the above poly(ketene acetals) were found to be of rather low molecular weight (dP ~ 20) as estimated by end-group analysis[2a,b] or vapor pressure osmometry.[2b] We modified McElvain's procedure to obtain a high molecular weight poly(hexyl ketene acetal)

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[1] Proceedings of ICSM '88. *Synth. Met.* **1989**, *28*, C1–C886, D1–D740; **1989**, *29*, E1–E574.

[2] (a) Johnson, P. R.; Barnes, H. M.; McElvain, S. M. *J. Am. Chem. Soc.* **1940**, *62*, 964. (b) Dunn, D. J.; Plesch, P. H. *Makromol. Chem.* **1974**, *175*, 2821.

[3] Olah, G. A., private communication and preprint, 1989. See accompanying paper in this issue.

[4] Marvel, C. S.; Denoon, C. E. *J. Am. Chem. Soc.* **1938**, *60*, 1045.

[5] Oda, R.; Munemiya, S.; Okano, M. *Makromol. Chem.* **1961**, *43*, 1961.

[6] Dynamit Nobel, AG. Neth. Appl. 6516487, 1964; *Chem. Abstr.* **1966**, *65*, 18780e.

[7] McElvain has hydrolyzed an oligomer of poly(ketene diethyl acetal) under extreme conditions (hot, concentrated sulfuric acid)[2a] and, not surprisingly, obtained an essentially intractable solid.

[8] Lal, J. *J. Polym. Sci.* **1959**, *41*, 399.

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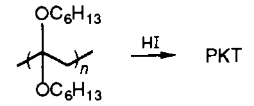
Table I. Physical Properties of PKT

IR (KBr), ν	^{1}H NMR (500 MHz, DMF-d_7), δ	^{13}C NMR (DMF-d_7), δ (ppm)	elem anal.	reduced viscosity (1/g dL), η	UV-vis (DMSO), nm
3700-2000 (br, vs), 1730 (w), 1650 (vs), 1595 (vs), 1400 (s), 1165 (s), 1100 (m), 940 (m), 862 (m)	9.8-11.3 (br m, 0.5 H, enol, phenol), 7.10-5.40 (m, 1.67 H, enol and aromatic CH), 4.69-3.30 (m, 2 H, interketone methylene)	clusters of resonances at 198, 178, 157-163, 136 (br), 113.5-115; peaks at 101.2, 46.0, 36.5	calcd for C_2H_2O: C 57.13; H, 4.80 calcd for $C_{17}H_{16}O_7$: C, 61.44; H, 4.82 found: C, 61.35; H, 5.11	0.1 (c = 0.36% w/w, DMF)	tail to 650, 365 (sh), 285; tail to[a] 820, 430, 355, 285; tail to[b] 720, 425 (sh), 350 (sh), 280, 240[c]

[a] Upon addition of 0.1 mL of 5% ethanolic KOH. The original spectrum is restored upon neutralization with acid. [b] Film on quartz. [c] Absorption too high to measure accurately.

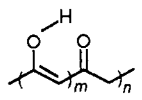
Scheme I



($\bar{M}_w \sim 720000$, poly(styrene) equivalent via GPC),[9] which we converted to the fully characterizable PKT.

Scheme I, below, describes the hydrolytic preparation of PKT in cyclopentanone/water (2:1) with 57% aqueous HI at 80 °C for 5-15 h, depending on the molecular weight of the precursor polymer.

The crude polymer was obtained as reddish-brown solid. Purification by extraction with hexane [to remove incompletely deprotected poly(ketal), hexyl iodide, hexyl alcohol and traces of iodine], followed by repeated reprecipitation from DMF with ether, afforded a dark brown-black solid in 86% yield. The polymer is soluble in DMSO, DMF, TFA, and pyridine, is partially soluble in propylene carbonate and 1:1 acetone/water, and is insoluble in CH_3NO_2, H_2O, Et_2O, MeOH, toluene, and THF. In agreement with the proposed structure, it is also soluble in 5% aqueous and 5% ethanolic KOH. The important characterization properties of this polymer are collected in Table I. As can be seen from the table, all spectroscopic (particularly ^{1}H NMR) data are consistent with the structure of PKT as depicted below, but the elemental analysis indicates loss of one molecule of water for every eight monomer units, tantamount to formation of an aromatic ring for every 17 carbon atoms.[10,11] Infrared spectroscopic evidence (3700-2000, 1730, 1650, and 1595 cm^{-1}), which is in excellent agreement with the infrared spectrum (under identical conditions) of 2,4,6-heptanetrione,[12] supports the above keto-enolic structure. There is a dramatic, reversible red shift in electronic absorption with increasing pH (see Table I), a property also exhibited by 2,4,6-heptanetrione.[12] Thermal analysis indicates that the polymer is stable up to ~200 °C. Between 200 and ~850 °C, there is a 43% weight loss (TGA, N_2 atmosphere), in good agreement with loss of one molecule of water/monomer unit. The residue from the TGA measurement exhibits a two-probe room temperature conductivity, σ, of ~2 S cm^{-1}. Graphite has $\sigma \sim$ 0.2 S cm^{-1} under the same conditions. The pristine polymer (powder) is an insulator with $\sigma < 10^{-8}$ S cm^{-1}. Exposure of the powder to iodine vapor increases the conductivity by only ca. 4 orders of magnitude ($\sigma \sim 10^{-4}$ S cm^{-1}). The pure polymer has essentially no unpaired spins; two superimposed, weak signals (1 spin/74000 monomer units or 1.3×10^{-5} spins/mol of monomer), $g = 2.0031$, $\Delta H_{pp} = 4.8$ G and ~12 G, indicating a minor spin impurity delocalized and localized, respectively, and located near oxygen.



$m \sim 0.63$, $n \sim 0.37$

The polymer forms brittle, dark, transparent thin films when cast from solution but forms flexible, stable, transparent composite films with poly(vinylpyrrolidone) when cast from homogeneous solution in DMF. Nonlinear optical properties as well as other physical properties (in situ spectroscopy, doping, etc.) of these films are being actively investigated.

Acknowledgment. We thank the AFOSR and the ONR for generous support of this work.

Supplementary Material Available: Complete spectroscopic characterization of freshly prepared 2,4,6-heptanetrione including IR (neat and in $CHCl_3$ solution), ^{1}H NMR in DMF-d_7 and $CDCl_3$, ^{13}C NMR in DMF-d_7 and $CDCl_3$, UV-vis, UV-vis as a function of pH, and MS (1 page). Ordering information is given on any current masthead page.

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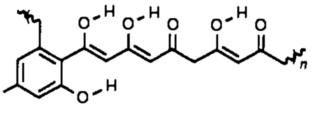
[9] Khemani, K. C.; Askari, S.; Wudl, F., submitted to *Macromolecules*.

[10] A possible structure, which fits the elemental analysis and spectroscopy, is depicted below. The aromatic rings are very likely randomly distributed with extensive runs of conjugated double bonds (electronic absorption in the visible, IR absorption at 1650 and 1595 cm^{-1}) and could be a combination of substituted resorcinols (depicted), trihydroxynaphthalenes, tetrahydroxyanthracenes, etc. Some of the ^{13}C resonances at 113-115 ppm, besides corresponding to enol carbon atoms, also coincide with assignments to aromatic carbon atoms ortho to a hydroxy substituent.



[11] Hydroxy aromatic ring formation from open-chain poly-1,3-ones is well precedented: Gilbreath, S. G.; Harris, C. M.; Harris, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 6172.

[12] Khemani, K. C., unpublished results on spectroscopy of freshly prepared 2,4,6-heptanetrione, available in the form of supplementary material (see Supplementary Material Available).

Glycoconjugated Tetrapyrrolic Macrocycles

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The superstructured models of active site of hemoproteins[1] can allow variation of facial cavity size for synthetic control of the ligand binding.[2] We report the first examples of another class

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