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Friedel–Crafts Dehydrohalogenative Polymerization of Acetyl and Enolizable Substituted Acetyl Halides to Polyketenes (Poly(oxyacetylenes))[1a]

George A. Olah,* Elazar Zadok,[1b] Ronald Edler,[1c]
Douglas H. Adamson, Walter Kasha, and
G. K. Surya Prakash

Donald P. and Katherine B. Loker Hydrocarbon
Research Institute and Department of Chemistry
University of Southern California
Los Angeles, California 90089-1661

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In polymer chemistry the possibility of finding easily available, inexpensive new monomers of substantial utility is extremely limited. We would like to report now the unexpected finding that acetyl chloride and substituted enolizable acetyl halides containing at least one α-hydrogen atom readily undergo Friedel–Crafts dehydrohalogenative polymerization to polyketenes.

The polymerization of ketenes has been extensively studied since the pioneering work of Staudinger[2] and Wedekind.[3] As shown inter alia by Natta et al.[4] the polymerization of ketene generally gives polyketone–ester type polymers and not polyketene. Oda et al.[5] reported that in the presence of boron trifluoride, ketene or diketene gave low yields of an amorphous light brown polymer of low molecular weight (MW ~2000) which they believed was polyketene, although insufficient evidence was provided to substantiate the claim.

In the course of our studies on stable carbocations we have observed[6] that the acetyl cation can undergo deprotonation to ketene not unlike the *tert*-butyl cation to isobutylene. The in situ

$$CH_3CO^+ \rightleftharpoons CH_2{=}C{=}O + H^+$$

$$(CH_3)_3C^+ \rightleftharpoons (CH_3)_2C{=}CH_2 + H^+$$

formed ketene then results in formation of acetoacetyl and diacetoacyl cations.[7] In the Nafion-H catalyzed acylation of aromatics with acyl chlorides we have also observed that acetyl chloride failed to give aromatic ketones and instead formed ketene, which was polymerized by the solid acid.[8] However, we have not followed up these observations till now.

All our attempts to polymerize ketene itself to polyketene resulted only in polymers of mixed ketone–ester nature with low molecular weights as well as dehydroacetic acid and pyrone derivatives.

Interested in the possibility of cationic polymerization of ketene formed in situ by the deprotonation of the acetyl cation, we allowed acetyl chloride to react in the presence of 10 mol % of Lewis acid halide ($AlCl_3$, $FeCl_3$, $ZnCl_2$, $TiCl_4$, BF_3, $SbCl_5$) catalyst generally at 150 °C for 20 h (experiments from 2 to 100 h were also carried out) in a Monel pressure autoclave. After depressurizing the formed HCl gas and washing the product with 10% aqueous HCl and water, a shining black polymer was obtained, which was dried in vacuum. Table I summarizes the results.

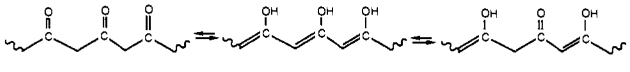
The same polymer was also obtained when methyl chloride was allowed to react in the presence of CO and $AlCl_3$ as catalyst, indicating in situ formation of acetyl chloride involving methylation of CO by the $CH_3Cl \rightarrow AlCl_3$ complex and its subsequent dehydrochlorinative polymerization.

Table I. Friedel–Crafts Lewis Acid Halide Catalyzed Polymerizations of Acetyl Chloride

Lewis acid	reaction time (h)	reaction temp (°C)	yield of polyketene[a] (%)
$AlCl_3$	20	100	
$AlCl_3$	2	150	4
$AlCl_3$	20	150	25
$AlCl_3$	72	150	43
$AlCl_3$	100	150	59
$FeCl_3$	20	150	25
$ZnCl_2$	20	150	23
$ZnCl_2$	65	150	39
$TiCl_4$	20	150	35
BF_3	20	150	62
$SbCl_5$	20	150	75

[a] Based on the amount of acetyl chloride used.

The obtained shiny black polymers are infusible even at 300 °C and highly insoluble in organic solvents. Due to their insoluble nature it was not possible so far to determine their molecular weight. Spectroscopic data show the polyconjugated nature of the polymers. IR absorptions at 3400, 1718, 1655, and 1600 cm^{-1} can be assigned to polyketene, with a keto–enol equilibrium structure. This agrees with the IR spectrum of 2,4,6-heptanetrione[9] which is known to exist in a keto–enol equilibrium. Further evidence for the keto–enol equilibrium was obtained from 15 MHz solid-state CPMAS ^{13}C NMR spectra. A broad absorption at around $\delta^{13}C$ 35 is assigned to the CH_2 group in the keto form and an envelope of absorptions ranging from $\delta^{13}C$ 127 to 210 to the enolic, carbonyl, and double bond carbons. From the solid-state ^{13}C NMR data the keto–enol equilibrium is estimated as about 30:70%, with the conjugated enolic polyene form predominating.



We were also able to carry out UV–vis measurements on polymer films as well as measure third-order nonlinear susceptibilities, $X^{(3)}$ based on optical susceptibility of these films.[10] The onset of absorption at about 2.0 eV in the UV–vis linear absorption spectra (both at room and liquid nitrogen temperature) indicates a conjugated π-system[11] in accord with the IR and NMR data. The broad onset of the absorption suggests delocalized π-units separated by nonconjugating groups.[11] The polymer also showed an ESR signal[11] with a g factor of 2.0031 (slightly higher than the g factor for pure *trans*-polyacetylene of 2.002634).[12] This is in agreement with an extended polyene nature and indicates that the free electron in the polymer has a significant propensity of residing on the oxygen atoms. The peak-to-peak line width ΔH_{pp} is 11.25 G, in the same range as that observed for *trans*-polyacetylene (14.3 G).[12]

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[1] (a) Ionic Polymerization. 6. For Part 5 see: Olah, G. A.; Farooq, O.; Li, C. X.; Farnia, M. S. M. F.; Aklonis, J. J. *Macromolecules*. In press. (b) On sabbatical leave from the Department of Chemistry, Governmental Research Institute, P.O. Box 14299, Tel Aviv, Israel. (c) Post-Doctoral fellow supported by the Gottlieb Daimler und Karl Benz Foundation, Federal Republic of Germany.

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[4] Natta, G.; Mazzanti, G.; Pregaglia, G.; Binaghi, M.; Peraldo, M. *J. Am. Chem. Soc.* **1960**, *82*, 4742.

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[8] Olah, G. A.; Malhotra, R.; Narang, S. C.; Olah, J. A. *Synthesis* **1978**, 672.

[9] Bethell, J. R.; Maitland, P. *J. Chem. Soc.* **1962**, 3751.

[10] Films were prepared directly on glass slides (separated by 0.025-mm Teflon spacers) by polymerizing the acetyl halides directly on them in a Monel vessel pressure. Measurements were carried out by Prof. R. Hellwarth et al. by using the "four wave mixing" method with three input lasers of wavelength of 532 nm. Calculated $X^{(3)} = 1.15 \times 10^{-9}$ (esu). Films prepared without spacers with assumed thickness of 1 μm gave calculated $X^{(3)}$ values of 1.5×10^{-9}/esu. The thickness of the films, however, is not well-established, and the films themselves are sensitive to the method of preparation. Thus these preliminary data are tentative and further studies are needed. Prof. A. J. Heeger and D. McBranch attempted to carry out third harmonic generation (THG) experiments at a wavelength of 1.06 μm at room temperature. No detectable THG signal was seen, whereas THG from silicon was readily measured. Reflected THG from the polymer film was thus at least 50 times smaller than from silicon. Using the estimate of linear index of reflection of 1.7 for the polymer a value of $X^{(3)}$ of $\leq 1.10^{-12}$ (esu) is obtained. Better films of higher molecular weight polymer are needed before any further evaluation of these seemingly contradictory results can be made.

[11] Measurements were kindly carried out by Profs. F. Wudl and A. J. Heeger et al., Institute for Polymers and Organic Solids, University of California, Santa Barbara, CA.

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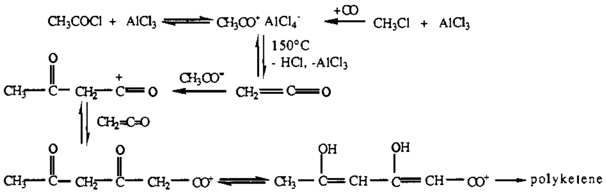
We suggest that the polymerization involves initial ionization of the acetyl chloride–aluminum trichloride complex to the acetyl cation followed by slow deprotonation at the reaction temperature to form ketene in situ. Ketene is then immediately acylated by acetyl cation or subsequently by the growing 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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(15) Khemani, K. C.; Wudl, F. accompanying communication.

(16) These measurements were carried out by Dr. E. Zadok in Israel.

Poly(ketene) (PKT)

K. C. Khemani and F. Wudl*

Institute for Polymers and Organic Solids
Departments of Physics and Chemistry
University of California
Santa Barbara, California 93106

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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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