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High Molecular Weight Poly(ketene dihexyl acetal): Anion Effect in a Cationic Polymerization

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ABSTRACT: We describe the preparation and full characterization of the title polymer. High molecular weight material was obtained with cadmium triflate as catalyst. The PKHA is a white solid that is soluble in most polymer solvents but precipitates out of THF/methanol in *crystalline* form. The experimental procedure for the conversion of the polymer to polyketene (PKT) is presented, along with the thermal and electrical properties of both polymers.

Introduction

Sixty years ago, McElvain discovered that the best catalyst to polymerize ketene diethyl acetal cationically was cadmium chloride.[1] In the intervening years, several researchers confirmed this result[2] and extended it to the polymerization of other symmetrically and unsymmetrically substituted ketene acetals. In all cases (a) the polymer was insoluble and (b) the polymer was of low molecular weight. The first observation was initially ascribed to possible cross-linking but Lal[2b] has shown that the insolubility is likely due to the high degree of crystallinity of the polymer. The second observation was ascribed to efficient chain transfer and/or termination steps.[2a]

We were interested in obtaining a high molecular weight poly(ketene acetal) because we wanted to convert it, under mild conditions, to polyketene (PKT). We recently reported that indeed one can prepare PKT by this approach.[3] Here we report our observations on the preparation, polymerization, and full characterization of the polymer of ketene dihexyl acetal (PKHA). We also give a detailed experimental procedure for the conversion of PKHA to PKT.

Results and Discussion

Preparation of Ketene Dihexyl Acetal. We wanted this monomer because we reasoned that the large, flexible hexyl substituents would serve two functions: (i) they would increase the stability of the monomer toward hydrolysis due to the increased hydrophobicity and (ii) they would render the polymer soluble in common solvents such as THF and chloroform. The simplest method to prepare this monomer was found to be alkoxide exchange of commercial bromoacetaldehyde diethyl acetal with hexanol under *p*-toluenesulfonic acid (PTSA) catalysis, followed by elimination with potassium *tert*-butoxide. The alkoxide interchange proceeded in 92% yield and the elimination reaction in 81% yield. The monomer is a colorless, mobile liquid, that can be purified by distillation under reduced pressure and is stable at −10 to −5 °C for extended periods of time. All spectroscopic properties are in accord with the expected structure (see Table I and the Experimental Section).

Polymerization Conditions. First we repeated McElvain's experiments with cadmium chloride as initiator. The salt was dried rigorously and all usual precautions to obtain high molecular weights were followed, including neutralization of the glass surfaces with ammonia, prior to thorough drying. Variations in temperature, monomer concentration, and solvent always gave low molecular weight products.

Table I
Properties of PKHA

IR, cm^{-1}, (film on NaCl plate)	2960 (s), 2220 (s), 2870 (s), 1470 (m), 1385 (m), 1360 (m), 1230 (m), 1170 (s), 1080 (s), 1060 (s)
^{1}H NMR, ppm, (benzene-d_6)	1.05 (br, 6 H), 1.47 (br, 8 H), 1.65 (br, 4 H), 1.87 (br, 4 H), 3.40 (br, 2 H), 3.87 (br, 2 H), 4.00 (br, 2 H)
^{13}C NMR, ppm, (benzene-d_6)	104.82, 60.95–60.81, 37.51–37.61, 32.89–32.66, 31.49, 26.95, 23.35–23.06, 14.40–14.35
elem anal.	calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.27; H, 12.19
viscosity, THF solvent	intrinsic, $[\eta]_{22 °C}$ = 3.55; reduced viscosity for a 0.5% solution in THF $\eta_r^{22 °C}$ = 16.41 dL/g
UV–vis	232 (s), 249 (w), 255 (w), 260 nm (w)
$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ from GPC = 150 000; $\bar{M}_w$ from light scattering = 3×10^5; $\bar{M}_w/\bar{M}_n$ = 2.0
conductivity of TGA residue	two-probe method, σ_{rt} = 2.63 S cm^{-1}; graphite conductivity (National Carbon Co.; lot no. 2-50; high-purity graphite), σ_{rt} = 0.12, 0.25 S cm^{-1}

After many attempts with different cadmium salts, we concluded that chain termination may be caused by quenching of the propagating cationic site by the nucleophilic chloride.[4] The expected reactions in the polymerization of ketene dialkyl acetal initiated by $CdCl_2$ are depicted in Scheme I, where step 1 is the usual initiation (E^+, electrophile), step 2 the usual propagation, and step 3 termination by chloride anion.

This working hypothesis seems to be correct because substitution of cadmium chloride by cadmium triflate[5] immediately produced higher molecular weight material. The best conditions were found to be acetonitrile, −23 °C, and mechanical stirring, 4.5 h, followed by workup. Material produced under these conditions was a white powder with the properties summarized in Table I. We were surprised that $Cd(OTf)_2$ had not been reported before. We prepared the latter by reaction of $CdCl_2$ with AgOTf.

Polymer Properties. The polymer is a white powder that is soluble in most common polymer solvents such as tetrahydrofuran, chloroform, chlorobenzene, methylene

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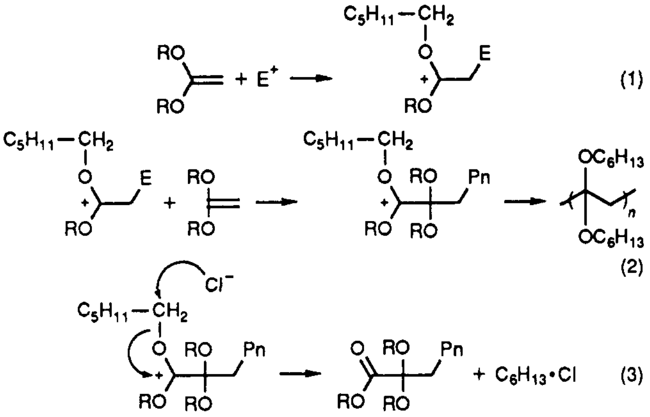
Scheme I



chloride, etc. and insoluble in methanol and ethanol. As can be seen from the table, the polymer is indeed a macromolecule and not an oligomer. Its reduced viscosity of 16.41 is a factor of 3 times that reported for poly(ketene dibutyl acetal)[2b] prepared via $CdCl_2$. The molecular weight distribution of the polymer, depending of the measurement method, gives a polydispersity index of 2.0 ($\bar{M}_w = 3 \times 10^5$ from light scattering) or 4.8 ($\bar{M}_w$ from GPC). Assuming that the $\bar{M}_w$ determination by light scattering is the most accurate, the polydispersity of this material is ~2. Depending on the method used, the DP of this polymer is $\sim 10^3$ ($\sim 1.2 \times 10^3$ to $\sim 3 \times 10^3$).

Solution proton NMR spectroscopy revealed that, at room temperature, the resonance of the methylene α to the acetal oxygen appeared as a doublet (δ 4.00 and 3.87). This doublet was found to collapse to a singlet at 60 °C. This result indicates that either (i) the two methylene hydrogens on the same carbon atom find themselves in different environments at room temperature, yet there are no asymmetric centers near the methylene in question, or (ii) each of the geminal alkoxides of the acetal moiety is in a different environment. The simplest explanation is that the polymer exists as a tight coil in solution at room temperature. To determine if this implied rigidity in solution induced order in the condensed state, we determined the X-ray powder pattern of a *reprecipitated*, unprocessed sample; indeed, as can be seen in Figure 1, this polymer has a high degree of crystallinity. However, the solid appears to be centrosymmetric, since it does not exhibit nonlinear optical behavior when attempts were made to measure second harmonic generation efficiency. The strong tendency toward crystallization would explain why films cast from THF solution are brittle.

In Figure 2 we show the thermal properties of the title polymer. As can be seen, it is stable only up to ~240 °C. At that temperature it undergoes a catastrophic depolymerization to produce volatile fragments. Closer examination of the TGA reveals that the decomposition occurs in stages with approximately 60% weight loss, which corresponds roughly to loss of one hexyloxy group for the first stage.[6] A second decomposition stage at ~400 °C corresponds to a total weight loss of 70%. Finally, heating beyond 730 °C gives a residue that is ~10% of the original mass. The latter is a shiny black solid with powder conductivity higher than graphite as measured under identical conditions (see Table I).

Many conditions for the conversion of the title polymer to PKT were attempted. Most resulted in unacceptable amounts of chain scission. Eventually we discovered that the best method was aqueous hydroiodic acid in cyclopentanone at 80 °C for 5 h and 25 °C for 16 h. The resulting polymer had undergone some chain scission and condensation (loss of water as determined by elemental analysis).[3]

Experimental Section

Preparation of Ketene Dihexyl Acetal, $CH_2{=}C(OHexyl)_2$. A mixture of bromoacetaldehyde diethyl acetal (Aldrich) (77 mL, 507 mmol), hexyl alcohol (Aldrich) (445.5 mL, 3550 mmol), and *p*-toluenesulfonic acid monohydrate (Aldrich) (20 g, 105 mmol) was heated for 15 h at 85 °C, under nitrogen, in a 1-L round-bottom flask fitted with a reflux condenser. A distillation unit was then attached to the flask and the temperature raised to 128 °C. The distillate (mostly ethanol) was discarded. When no more liquid came over, the temperature was raised to 140 °C. Another 100 mL of distillate was collected and discarded. The reaction mixture was cooled to room temperature and then poured into water (500 mL). The mixture was extracted with ether (5 × 200 mL). The ether extracts were combined and dried ($MgSO_4$) and filtered and the solvent was evaporated. The liquid so obtained (~400 mL) was subjected to vacuum distillation (0.2 mm/80 °C bath temperature) and the distillate (hexyl alcohol, ~250 mL) was discarded. The light brown liquid remaining in the still pot was further distilled and the product, 2-bromoacetaldehyde dihexyl acetal, collected as a colorless liquid (145 g, 92%), bp 140–142 °C (1.02mm): IR (neat) ν (cm^{-1}) 3010 (vs), 2980 (vs), 2910 (s), 1500 (m), 1450 (w), 1405 (w), 1375 (m), 1210 (m), 1150 (vs), 1090 (vs), 1050 (s), 950 (w), 750 (m), 705 (m); ^1H NMR ($CDCl_3$) δ 0.89 (t, 6 H), 1.61–1.75 and 1.42–1.28 (both multiplets, 16 H), 3.64–3.60 (m, 2 H), 3.51–3.47 (m, 2 H), 3.36 (d, 2 H), 4.66 (t, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.13, 22.73, 25.92, 29.83, 29.97, 31.75, 66.95, 101.82.

tert-Butyl alcohol (Fisher) (500 mL) was dried with potassium (5 g) in a round-bottom flask at 80–85 °C for 12 h followed by distillation under argon atmosphere. To dry *tert*-butyl alcohol (321.3 mL, 3.4 mol) contained in a 500-mL round-bottom flask, clean potassium (15.16 g, 0.39 mol) was added under argon and the mixture refluxed and stirred at 100 °C in an oil bath until all the potassium had dissolved (~5 h). The bromo dihexyl acetal prepared above (100 g, 0.32 mol) was then quickly added to the above *tert*-butoxide/*tert*-butyl alcohol solution, under argon, using an addition funnel. The reaction mixture became milky in 10 min. The mixture was stirred and refluxed further at 100 °C for 36 h. After this time, a distillation unit containing a built-in 8″ Vigreux column was attached to the reaction flask and *tert*-butyl alcohol distilled off smoothly under ambient pressure, bp 84 °C (oil bath temperature = 128 °C). When *tert*-butyl alcohol stopped distilling over, the temperature of the oil bath was lowered to 80 °C and the remaining *tert*-butyl alcohol distilled under vacuum (1 mm). A viscous light brown liquid containing solid KBr was left in the still pot. The product was recovered from this by fractional distillation under high vacuum [bp 89–91 °C (0.3 mm)] (oil bath temperature = 155–165 °C). The product was redistilled and collected as a colorless liquid [bp 89–91 °C (0.3 mm)] (60.1 g, 81%): ^1H NMR ($CDCl_3$) δ 0.60–2.00 (m, 22 H), 3.08 (s, 2 H), 3.74 (t, 4 H); IR (neat) ν 2950 (vs), 2880 (s), 1660 (vs), 1480 (m), 1415 (w), 1390 (w), 1290 (vs), 1210 (w), 1075 (s), 1025 (s), 912 (w), 715 (s) cm^{-1}.

Preparation of Cadmium Triflate, $Cd(OSO_2CF_3)_2$. To a solution of $CdCl_2$ (Aldrich) (1.726 g, 9.42 mmol) in deionized water (15 mL), was added dropwise, with stirring, a solution of silver triflate (Aldrich) (4.84 g, 18.84 mmol) in water (25 mL). After complete addition, the stirring was stopped and the precipitate allowed to settle. Aqueous silver triflate solution was trickled down the side of the vessel dropwise until no further precipitation was observed. The precipitated silver chloride was filtered and the filtrate evaporated on a rotary evaporator. The white solid so obtained was dried at 110 °C (0.25 mm) (48 h) and then further at 120 °C (0.25 mm) (48 h) to constant weight (3.3 g, 85%): IR (KBr) ν 2910 (vs), 1460 (s), 1370 (s), 1225 (s), 1060 (m), 720 (w) cm^{-1}.

Polymerization of Ketene Dihexyl Acetal. A 10-mL three-neck flask (flame dried under argon) was fitted with a mechanical stirrer and two rubber septa. A constant slow flow of dry argon was maintained in the flask. Dry cadmium triflate (1 mg, 2.4×10^{-6} mol) as prepared above was added to the flask. The flask containing the catalyst was cooled to −23 °C by using a CCl_4/dry ice bath. The mechanical stirrer was started and the

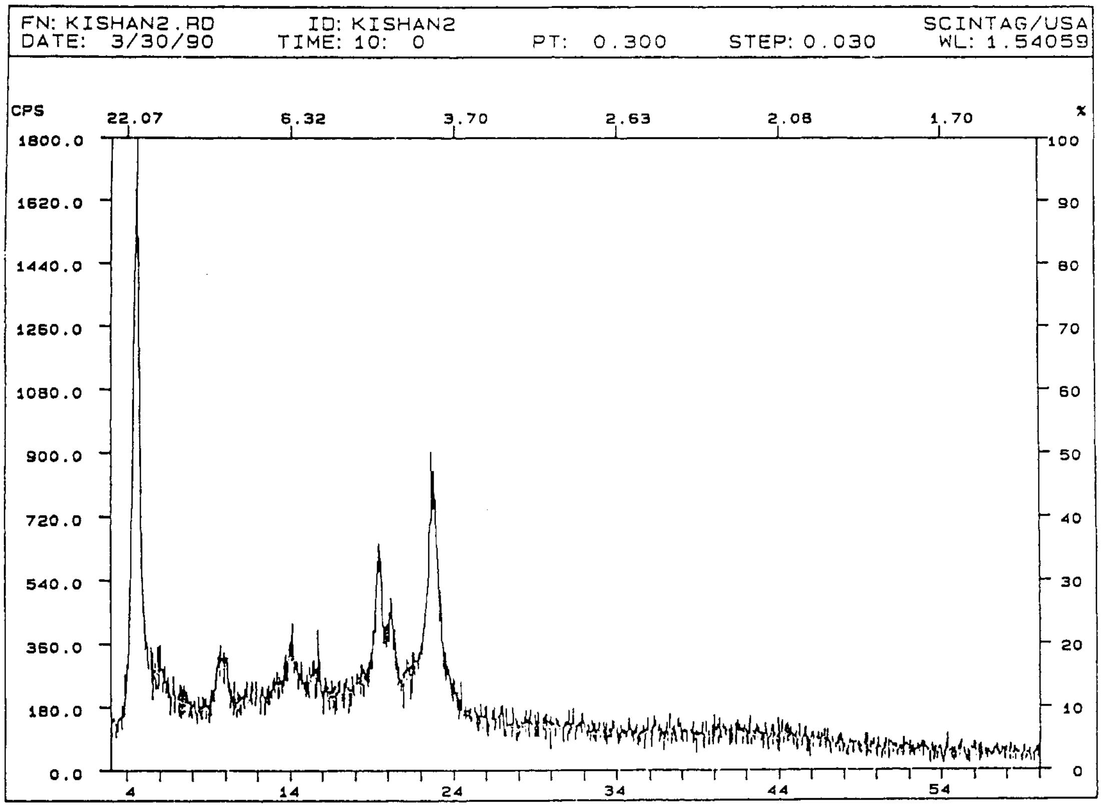


Figure 1. X-ray powder pattern of a freshly precipitated sample of PKHA.

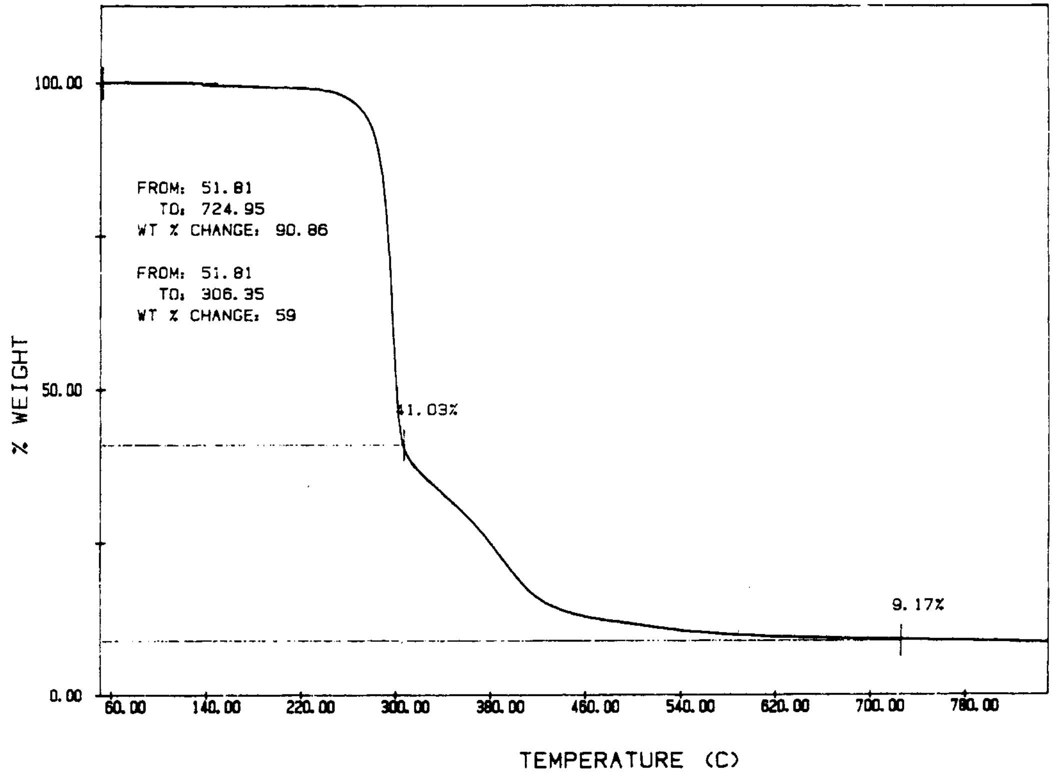


Figure 2. Thermal gravimetric analysis of PKHA under nitrogen; heating rate, 10 °C/min.

monomer (4.3 mL) was added via a syringe. The reaction mixture became viscous after 10 min and solid chunks of the polymer were visible after 30 min. The mixture was allowed to (0.5 h) thaw slowly to room temperature and then stirred at this temperature for 3.5 h. The white polymeric solid so obtained was transferred (using THF) to an Erlenmeyer flask (125 mL) and dissolved in hot, dry THF (60 mL). Addition of acetone to the polymer solution precipitated the polymer, which was recovered by centrifugation. The process of dissolution in THF followed by precipitation with acetone was repeated once more. The recovered polymer was finally dried at room temperature under high vacuum (0.2 mm) (yield = 4 g). Anal. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.27; H, 12.19. For viscosity measurements, a Cannon-Ubbelohde constant-pressure viscometer was used. Solutions (0.50%, 0.25%, 0.125%, and 0.0625% w/w) of the polymer were made in dry THF, and the efflux time was recorded. From a plot of c versus η_{sp}/c, the intercept gave the intrinsic viscosity for the polymer of $[\eta] = 3.55$ P at 22 °C ($\eta_{red} = 16.41$ dL g^{-1}, $c = 0.5\%$ w/w). One could use the Mark–Houwink–Sakurada relationship $[\eta] = K\bar{M}_w^{\alpha}$, but there are no good model polymers for literature values of the exponent α.[7] Therefore $\bar{M}_w$ values from light scattering were used to determine the polydispersity (see Table I).

A Varian 5000 liquid chromatograph fitted with TSK-GEL GMH6 column and a SHODEX RI detector was used for GPC determinations. THF (HPLC grade, Fisher) (flow rate = 1 mL/min) was used as solvent. A plot of elution time versus $\bar{M}_n$ was created for polystyrene standards of known molecular weights ($M_n = 3.6 \times 10^3, 1.1 \times 10^5, 4.7 \times 10^5, 2.7 \times 10^6$) (Waters Associates, Milford, MA), and the retention time for poly(ketene dihexyl acetal) of 9.8 min was used to estimate its $\bar{M}_n$ at 150 000.

A Wyatt Technology Corp.'s "DAWN Model B" instrument was used for light scattering measurements on solutions (0.1%, 0.2%, 0.3%, 0.4% w/w) in dry THF. The molecular weight, M_w, was estimated from the Zimm plot at 3×10^5. Thermogravimetric analysis (TGA) with a heating rate of 10 °C/min showed that the polymer was stable up to 230 °C. Weight loss from 50 to 306 °C (notable inflection at 306 °C) was found to be 59%; weight loss from 50 to 725 °C was found to be 91% (expected weight loss for the loss of all side chains and the interketone methylene hydrogens = 89.5%). The sample recovered from the TGA experiment was a shiny black graphite-like film that had a two-probe conductivity of $\sigma_{rt} = 2.6$ S cm^{-1}; commercial graphite (National Carbon Co.), $\sigma_{rt} = 0.25$ S cm^{-1}.

Differential scanning calorimetry (DSC) of the polymer showed no heat flow up to 250 °C and an exotherm (decomposes) above this temperature. Visual examination of the thermal behavior was as follows: an open-ended capillary tube containing the polymer was put in a melting point apparatus and the polymer was observed to constrict at ~70 °C, brown specks were visible at ~95 °C, a completely brownish solid was observed at ~150 °C, and red-brown liquid droplets were observed at ~210 °C; complete melting to a brown liquid was finally observed at ~250 °C.

Hydrolysis of Poly(ketene dihexyl acetal) to Polyketene (PKT). Poly(ketene dihexyl acetal) (5 g, 21.9 mmol, based on monomer formula weight) was placed in a 100-mL two-necked round-bottom flask mounted on a magnetic stirring base and fitted with a reflux condenser and a rubber septum. A static pressure of argon was maintained. To the polymer, cyclopentanone (Aldrich) (40 mL), and water (20 mL) were added via a syringe. Stirring was started and aqueous hydroiodic acid (57%, Aldrich) (10 mL, 75.8 mmol, 3.5 equiv) was added via a syringe. The mixture immediately became yellowish and turned red in 5 min. After 1 h of stirring at room temperature, the reaction flask was lowered into an oil bath and heated to 80 °C. Stirring and heating were continued for 5 h, after which time the mixture was allowed to cool to room temperature and left stirring at that temperature for 16 h. The reaction mixture was then poured into water (300 mL) and the mixture shaken vigorously in a 1-L separatory funnel. The aqueous layer was drained and the red oil washed again similarly with fresh water (400 mL). At this point the dark red oil solidified and was washed on a fritted funnel with more fresh water until the filtrate was free of all color. The reddish brown solid was then washed further with hexane until the filtrate became free of purple color. The dark red polymer was then dissolved in DMF (10 mL) and precipitated by adding Et_2O to the solution. It was recovered by centrifugation. This process of dissolving in DMF and precipitation with Et_2O was repeated two more times. The polymer was finally washed with fresh Et_2O. It was then dried under vacuum to give a shiny dark brown-black solid (0.8 g, 86%). Anal. Calcd for C_2H_2O: C, 57.13; H, 4.80. Found: C, 61.35; H, 5.11.

Thermogravimetric analysis (TGA) with a heating rate of 10 °C/min showed that the polymer was stable up to 200 °C. Weight loss from 50 to 800 °C was found to be 42.7% (estimated weight loss for the loss of one molecule of H_2O per ketene unit = 43%). The sample recovered from the TGA experiment was a shiny black graphite-like material that had a two-probe conductivity of $\sigma_{rt} = 2.0$ S cm^{-1}. Anal. Calcd for $C_{17}H_4O$: C, 91.10; H, 1.80. Found: C, 91.34; H, 1.97. The polymer was soluble in dimethylformamide, dimethyl sulfoxide, pyridine, trifluoroacetic acid, 5% ethoxide in ethanol, and 10% potassium hydroxide in water and insoluble in nitromethane, water, ether, methanol, toluene, and THF but partially soluble in aqueous acetone and propylene carbonate. UV–vis: (DMF) onset at ~650 nm, 270 nm (s), 285 nm (s), 365 nm (m). Upon adding 2 drops of 10% alcoholic KOH, a red shift is observed: onset ~770 nm, 440 nm (m), 365 nm (m); (DMSO) onset ~650 nm, 280 nm (s), addition of 2 drops of 10% alcoholic KOH causes a red shift, onset ~820 nm, 430 nm (m), 355 (s), 280 nm (m). Addition of 2 drops of concentrated hydrochloric acid restores the original spectrum. The polymer is insoluble in ethanol but addition of 4 drops of 7.5% EtOH/KOH causes complete dissolution: onset ~670 nm; λ_{max}, 450 nm (m), 372 nm (m), 250 nm (s), 222 nm (s); IR (KBr) ν (cm^{-1}) 3700–2000 (vbr, s), 1730 (w), 1650 (vs), 1595 (vs), 1400 (s), 1165 (s), 1100 (m), 940 (m), 862 (m) cm^{-1}; ^{1}H NMR (DMF-d_7) δ 9.8–11.3 (br m, 0.5 H, enol, phenol), 7.10–5.40 (m, 1.67 H, enol, Ar CH), 4.69–3.30 (m, 2 H, interketone methylene); ^{13}C NMR (DMF-d_7) clusters of resonances at 198, 178, 157–163, 136 (br), 113.5–115 and peaks at 101.2, 46.0, 36.5 ppm; ESR, two superimposed weak signals, $\Delta H_{pp} = 4.80$ and 12 G (~1 spin/16 000 units; upon compensation with NH_3 for 7 days, signal intensity reduces considerably to ~1 spin/74 000 units), $g = 2.0031 \pm 0.0004$.

Two-probe conductivity measurement of the undoped material exhibited a resistance of $>3 \times 10^7\ \Omega$. The same measurement on an I_2 vapor-doped sample at 25 °C for 16 h showed a conductivity of $\sigma_{rt} = 10^{-4}$–10^{-6} S cm^{-1}. Acid doping with dry HCl gas at 25 °C for 7 h gave a conductivity $\sigma_{rt} = 10^{-8}$ S cm^{-1}.

Composite Formation. For optical and nonlinear optical characterization, we needed thin films. PKA has poor mechanical properties such that free standing films cannot be easily produced. After many attempts to form composites for the improvement of mechanical properties, it was discovered that a DMF solution of polyketene afforded homogeneous blends with a DMF solution of poly(vinylpyrrolidone) (Aldrich, average MW 3.6×10^5). This homogeneous viscous solution was spin-cast to smooth homogeneous films on quartz plates. Results of measurements on these films will be presented elsewhere.

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(2) (a) Dunn, D. J.; Plesch, P. H. *Makromol. Chem.* **1974**, *175*, 2821. (b) Lal, J. *J. Polym. Sci.* **1959**, *41*, 399.

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(4) In ref 2a it is "tentatively" suggested that the anion in the initiators may *not* compete effectively in chain transfer or termination steps.

(5) Cadmium triflate was not used before as a cationic initiator. However, a number of triflates have been studied: Collomb, J.; Gandini, A.; Cheradame, H. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 489. Collomb, J.; Morin, B.; Gandini, A.; Cheradame, H. *Eur. Polym. J.* **1980**, *16*, 1135. We thank Prof. Plesch for these references.

(6) Isothermal pyrolysis at 280 °C produces a red-brown polymer whose structure and properties are being investigated and will be the subject of a future publication (Khemani, K., unpublished results).

(7) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; John Wiley: New York, 1979; Table 8.2, p 252.