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ARTICLE

Synthesis and Ring-Opening Polymerization of 5-Azepane-2-one Ethylene Ketal: A New Route to Functional Aliphatic Polyamides

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ABSTRACT: A functional derivative of ε-caprolactam, 5-azepane-2-one ethylene ketal or γ-ethylene ketal ε-caprolactam, has been synthesized by a very straightforward and highly efficient Beckmann rearrangement reaction. Homopolymers of this new monomer and its copolymers with ε-caprolactam have been synthesized by anionic ring-opening polymerization using *N*-acetyl-ε-caprolactam and NaH. The ketone groups can be easily released by deacetalyzation, and subsequent reaction leads to complete reduction to hydroxyl pendant groups. The ketone-containing (co)polymers respond sensitively to both thermal and photo-cross-linking in this novel class of materials. These new aliphatic polyamides bearing either ketone or hydroxyl pendant groups provide entries into a large number of application areas.

Introduction

Polyamides or nylons are extremely versatile engineering thermoplastics that encompass a broad range of applicability in industries. One of the most common types of polyamide is poly(ε-caprolactam), PCL, which is also known as nylon-6. The industrial production of PCL involves either water initiated (hydrolytic) or strong base initiated (anionic) ring-opening polymerization of ε-caprolactam. While the hydrolytic polymerization of ε-caprolactam is the most important for commercial production of PCL, high molecular weight polymer with defined end groups can be produced very rapidly via anionic polymerization.[1]

PCL prepared from ring-opening polymerization of ε-caprolactam possess excellent tensile, flexural, and compressive strengths as well as resistance to abrasion and chemicals due to a high degree of crystallinity.[1] Nevertheless, it is desirable to have aliphatic polyamides having functional groups along the chains in order to tune properties such as hydrophilicity, crystallinity, solubility, and elasticity; to promote (bio)adhesion, biocompatibility, and/or biodegradability; or to label the polymer by attaching other compounds pendant to the backbone. However, the shortage of polyamides bearing functional groups is a severe limitation to further progress in this field.

To date, there are only a few reports on polyamides that are formed from the ring-opening polymerization of ε-caprolactam derivatives with functional groups. Reimschuessel et al.[2] reported the synthesis and polymerization of β-carboxymethylcaprolactam. The synthesis of this monomer was accomplished in four steps starting from α-bromocaprolactam. The product of the thermal polymerization of β-carboxymethylcaprolactam gave poly[(2,2-dioxo-1,4-piperidinediyl)trimethylene] as a hard crystalline polymer with melting temperature of 280 °C. In other words, instead of polyamide with carboxylic acid pendant groups, a novel linear polyimide was obtained from isomerization polymerization.

Racemic and optically active γ-*tert*-butoxymethylcaprolactam was polymerized by Overberger et al.[3] The monomer was synthesized by a sequence of reactions starting from 4-benzoloxymethylcyclohexanol. The yields of racemic and optically active polymer from the anionic ring-opening polymerization of γ-*tert*-butoxymethylcaprolactam ranged from 10 to 56% with a number-average molecular weight of 3000 g/mol. Obtained polymers were treated to remove the *tert*-butyl protective group to yield polyamide with hydroxymethyl pendant groups. Although the hydroxymethyl-substituted polyamides were soluble in polar solvents such as methanol, ethanol, and 2,2,2-trifluoroethanol, they were not soluble in water.

A modified poly(ε-caprolactam) containing sulfonate pendant groups has been reported by Nijenhuis et al.[4] γ-Phenylsulfonate caprolactam was synthesized starting from 4-phenylcyclohexanone. Beckmann rearrangement of 4-phenylcyclohexanone oxime to yield lactam and sulfonization of the phenyl ring were accomplished in one step using concentrated sulfuric acid. Finally, the alkali salt of γ-phenylsulfonate caprolactam was prepared by addition of alkali hydroxide. The polymers were synthesized under hydrolytic ring-opening polymerization conditions. While the phenyl sulfonate pendant group did not affect the thermal properties of the polymer, it did lead to a higher zero shear melt viscosity.

γ-Carboxyethylcaprolactam and γ-aminoethylcaprolactam were used for the synthesis of hyperbranched aliphatic polyamides. Carboxy- and amino-functionalized caprolactams were prepared by a multistep synthesis starting from methyl 3-(4-hydroxyphenyl)propanoate. Carboxy- and amino-terminated hyperbranched polyamides were obtained by using acidolytic formation of poly(ε-caprolactam). Cross-linked fractions were observed on heating for 48 h for the carboxy system and 4 h for the amino system.[5]

As shown by these examples, the typical pathway to functional polymers is based on functional monomers which are capable of polymerization. The functional groups must be selected or protected in such a way that they do not interfere with the polymerization mechanism. The shortage of examples is generally due to difficulties in synthesis of new monomers which are generally obtained by rather complex and time-consuming procedures. The aim of this paper is to report an efficient route to a new monomer as a precursor for a novel class of (co)polyamides

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bearing ketone and/or hydroxyl groups on the polymer backbone.

Experimental Section

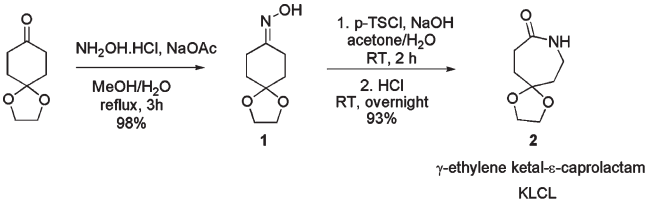
Materials. 1,4-Cyclohexanedione monoethylene ketal (>97%) and 2,2,2-trifluoroethanol (TFE) were purchased from Fluka. Hydroxylamine hydrochloride (99%), ε-caprolactam, and sodium borohydride (>98%) were purchased from Aldrich. *p*-Toluenesulfonyl chloride (*p*-TSCl) was purchased from Acros (>98%). Sodium acetate, sodium bicarbonate, sodium sulfate (anhydrous), sodium hydroxide, and all solvents were purchased from Fisher Scientific and used as received. ε-Caprolactam was recrystallized from acetone prior to use.

Synthesis of 4-Oximinocyclohexanone Ethylene Ketal (1). Hydroxylamine hydrochloride (85.3 mmol) and sodium acetate (85.3 mmol) were dissolved in 35 mL of H_2O in a 250 mL round-bottomed reaction flask. 1,4-Cyclohexanedione monoethylene ketal (77.5 mmol) in 145 mL of methanol was added. The temperature was then raised to 85 °C, and the reaction mixture was allowed to reflux for 2 h. After evaporation of methanol, 10 mL of H_2O was added, and the aqueous solution was transferred to an extraction funnel. The aqueous phase was extracted with ethyl acetate (3 × 100 mL). The combined organic phase was neutralized with aqueous $NaHCO_3$ (10 wt %) solution (3 × 50 mL), separated, dried over anhydrous Na_2SO_4, filtered, and evaporated. The product was further dried under vacuum at room temperature overnight. 4-Oximinocyclohexanone ethylene ketal (13.0 g, 98%) was obtained in the form of white crystals, mp 69.7 °C. Anal. Calcd for $C_8H_{13}NO_3$; C: 56.13 H: 7.65 N: 8.18. Found: C: 55.98 H: 7.59 N: 8.05. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.7 (s, 1H), 3.9 (t, 4H), 2.6 (t, 2H), 2.3 (t, 2H), 1.7 (t, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 158.3, 107.9, 64.3, 34.2, 32.9, 28.7, 21.0.

Synthesis of 5-Azepane-2-one Ethylene Ketal (2). Oxime **1** (60 mmol) was dissolved in 170 mL of acetone in a 500 mL round-bottomed flask charged with a magnetic stirrer. Addition of 60 mL of 4 N aqueous NaOH solution was followed by slow addition of *p*-toluenesulfonoyl chloride (108 mmol) dissolved in 170 mL of acetone. The reaction mixture was allowed to mix 2 h at room temperature. After the evaporation of acetone 40 mL of H_2O was added. The reaction mixture was then neutralized by dropwise addition of 4 N aqueous HCl solution. The reaction was allowed to proceed overnight at room temperature. The reaction mixture was transferred into an extraction funnel, and the product was separated by extraction with CH_2Cl_2 (5 × 200 mL). Combined organic phases were dried over anhydrous Na_2SO_4 and filtered, and the solvent was evaporated. 5-Azepane-2-one ethylene ketal, KLCL (9.6 g, 93%), was recrsytallized twice from acetone, mp 104 °C. Anal. Calcd for $C_8H_{13}NO_3$; C: 56.13 H: 7.65 N: 8.18. Found: C: 56.26 H: 7.71 N: 8.09. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.7 (s, 1H), 3.7 (s, 4H), 3.0 (t, 2H), 2.3 (t, 2H), 1.6 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 178.3, 108.6, 64.0, 38.7, 37.0, 32.5, 30.3. IR (KBr): ν 3214 (s), 2967 (w), 2896 (w), 1664 (s), 1448 (m), 1114 (s), 896 (m) 507 (w) cm^{-1}.

General Procedure for the Anionic (Co)polymerization. In a typical experiment, monomer or combined monomers (20 mmol) were weighed and added to a flame-dried polymerization tube. The system was purged with nitrogen for 30 min. After the addition of *N*-acetylcaprolactam (0.2 mmol) through a syringe, the polymerization tube was placed into an oil bath adjusted at 140 °C. The reaction mixture was maintained under stirring for 15 min at this temperature before the addition of NaH (0.2 mmol, 50 wt % dispersion in mineral oil). The polymerization was allowed to proceed for 3 h under N_2 atmosphere. After cooling down to room temperature, the homopolymer was ground to a powder and dispersed in methanol, stirred for 24 h, and filtered. The copolymers were ground and dispersed in CH_2Cl_2, stirred for 24 h, and filtered in order to remove unreacted monomers. The polymers were dissolved in TFE and precipitated into diethyl ether.

Scheme 1



General Procedure for the Deprotection of Ketone Groups. A sample of 0.2 g of (co)polymer was dissolved in 10 mL of aqueous HCl (4 wt %) solution. The mixture was maintained under stirring at room temperature overnight, during which the deprotected polymer precipitated from the solution. After neutralization with $NaHCO_3$, the polymer was filtered and washed with water several times. The white polymer powder was dried under vacuum at 50 °C. For the copolymers with high ε-caprolactam content (i.e., 75 mol %), deprotection of the ketone groups was performed using moist trifluoroacetic acid at room temperature. The deprotected polymer was then precipitated into water, filtered, and dried at 50 °C under vacuum.

General Procedure for the Reduction of Ketone Groups. A 1.0 g portion of (co)polymer was dissolved in 35 mL of a 5:2 v:v $CHCl_3$:TFE mixture in a 50 mL round-bottomed flask which had been dried and purged with N_2. $NaBH_4$ (0.1 g) was added into the reaction vessel quickly. The mixture was maintained under stirring at room temperature for 30 min. After filtration, the solvent mixture was evaporated. The polymer was dissolved in TFE and precipitated into diethyl ether. The white powder (co)polymers were filtered and dried under vacuum at 50 °C overnight.

UV Irradiation. Thin films of a ketone-containing homopolymer, P(KCL), were cast using TFE as a solvent. The films were dried under vacuum for 24 h and then placed into a quartz box which was purged with argon for 24 h prior to UV irradiation. The box was then placed under a medium-pressure mercury lamp with light intensity 40 mW/cm^2. The quartz box was continuously purged with argon during irradiation with UV light. The inside temperature of the quartz box was around 30 °C after 5 h of irradiation so thermal reaction did not occur.

Characterization. ^{1}H and ^{13}C NMR spectra were obtained in TFE:$CDCl_3$ (70:30 v:v mixture) using Varian Gemini 300 and ^{UNITY}INOVA 500 spectrometers operating at 300 or 500 MHz for proton and 75 or 125 MHz for carbon. Solution ^{13}C NMR spectra for the end-group analysis were collected on ^{UNITY}INOVA 500 MHz NMR operating at 125 MHz spectral frequency. NMR samples were prepared by dissolving polymers in a solvent mixture consisting of a 7:3 ratio of TFE to $CDCl_3$ to give low-viscosity solutions. To maximize signal-to-noise ratios, the samples were prepared at high concentrations (~25 wt %), and the number of scans was kept as high as 20 000 scans (~18 h). The number-average molecular weights of the polymers were calculated from the peak intensities of main-chain carbonyl and end-group carbonyl.

Solid-state NMR spectroscopy was performed on a ^{UNITY}INOVA 400 spectrometer using a standard Chemagnetics 7.5 mm PENCIL-style probe. Samples were loaded into zirconia rotor sleeves, sealed with Teflon caps, and spun at 4.0 kHz. The standard cross-polarization/magic angle spinning (CP/MAS) technique was used with proton decoupling implemented during data acquisition.[6] In addition, the TOSS technique was implemented to remove/minimize spinning side bands.[7] The acquisition parameters were as follows: ^{1}H 90° pulse width was 5.5 μs, cross-polarization contact time was 1.5 ms, dead time delay was 6.4 μs, acquisition time was 45 ms, and recycle delay between scans was 3 s.

FTIR spectra were recorded on an ATI-Mattson Galaxy 5000 FTIR spectrometer. Thermal analyses were performed on a TA

Table 1. Homopolymerization of KLCL Initiated by *N*-AcCL in Bulk at 140 °C

entry	[KLCL]/[*N*-AcCL]	[NaH]/[*N*-AcCL]	M_{ntheo}[a] (g/mol) ($\times 10^{-3}$)	polym time (h)	conv (%)	M_{nexp}[b] (g/mol) ($\times 10^{-3}$)
1	90	2.0	15.4	0.5	61	15.0
2	75	2.5	12.9	1	67	11.1
3	100	1.5	17.3	3	68	16.6
4	100	1.5	13.3	3	98	13.0

[a] $M_{n,theo}$: molecular weight calculated from monomer-to-initiator ratio. [b] $M_{n,exp}$: molecular weight determined from NMR end-group analysis.

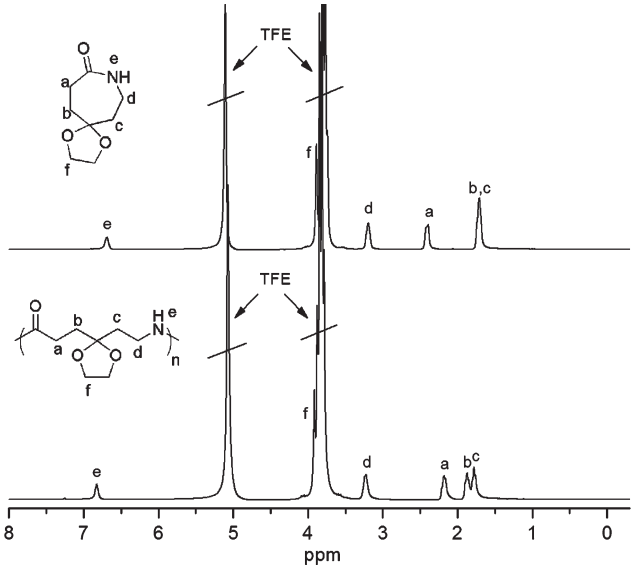


Figure 1. ^{1}H NMR spectra of KLCL (top) and P(KLCL) (bottom).

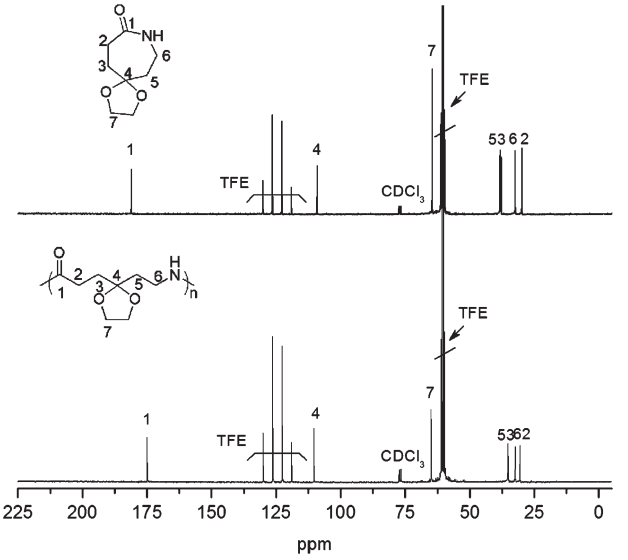


Figure 2. ^{13}C NMR spectra of KLCL (top) and P(KLCL) (bottom).

Instruments SDT 2960 TGA-DTA at 10 °C/min under nitrogen from ambient temperature to 600 °C and on a DSC 2920 at 10 °C/min under nitrogen from ambient to 250 °C. An Ubbelohde viscometer was used for the dilute solution viscosity measurements in TFE at 25 °C at low concentrations (in the range of 0.05−0.2 g/dL). The viscosity-average molecular weights were calculated using previously reported Mark−Houwink constants determined for poly(ε-caprolactam).[8] Elemental analyses were performed by Quantitative Technologies, Inc.

Results and Discussion

Synthesis of 5-azepane-2-one ethylene ketal (alternatively named as ethylene ketal substituted ε-caprolactam or KLCL) was accomplished through a modified Beckmann rearrangement reaction. The classic Beckmann rearrangement conditions require high temperatures and very strong protic acids such as concentrated or fuming sulfuric acid, trichloroacetic acid, or poly(phosphoric acid). In this study, traditional Beckmann rearrangement conditions led to undesired products. However, the synthesis of KLCL was successful in the presence of *p*-TSCl and sufficient NaOH(aq) to maintain neutrality. A 93% yield was obtained. This procedure is not only very efficient but also very mild because the reaction takes place at room temperature in a neutral medium. The schematic representation of the reaction pathway starting from the commercially available 1,4-cyclohexanedione monoethylene ketal is shown in Scheme 1.

The polymerization of KLCL was achieved by anionic ring-opening polymerization. The polymerization reaction was carried out in bulk at 140 °C using *N*-acetylcaprolactam (*N*-AcCL) and NaH, the ratios of which are given in Table 1. The polymerization was allowed to proceed under a N_2 atmosphere. Although the polymerization mixture became very viscous and solidified within 5 min, only 68% conversion after 3 h of polymerization was calculated from the ^{13}C NMR spectrum of the crude product. In contrast, ε-caprolactam (CL) shows 98% conversion under the same conditions. In general, the equilibrium monomer concentration appears to increase with the bulk of substituent on the seven-membered ring lactams.[9,10] Thus, the bulky ethylene ketal group might be limiting the conversion of KLCL.

The unreacted monomer was removed by extraction with methanol for 24 h. The complete removal of monomer was confirmed by ^{1}H and ^{13}C NMR spectra of the polymer after extraction. The ^{1}H and ^{13}C NMR spectra also showed that the ketal groups were stable toward the initiating and propagating species under these experimental conditions (Figures 1 and 2).

^{13}C NMR end-group analysis for molecular weight determination is a useful technique which has been used for many different nylons in our research group previously.[11,12] The molecular weights were calculated from ^{13}C NMR data using the relative intensity of the carbonyl peak (at 173.3 ppm, peak 4) of the *N*-acetyl end group resulting from *N*-AcCL co-initiator and the amide carbonyl peak (at 174.9 ppm, peak 3) of the monomer repeat units in Figure 3. Values obtained are in good agreement with values calculated from the monomer-to-initiator ratios (Table 1).

KLCL and CL were copolymerized using the same polymerization conditions, i.e., at 140 °C under N_2 atmosphere. The copolymer compositions as well as copolymer sequences were determined by ^{13}C NMR analysis. The carbonyl region and the aliphatic region of the ^{13}C NMR spectra of both homopolymers and their copolymers are given in Figure 4. There are four different amide carbonyl groups for the copolymers which is consistent with random copolymer composition; i.e., the peak at 174.9 ppm corresponds to KLCL units next to each other, the peak at 176.0 ppm corresponds to CL units next to each other, and the two peaks in the middle (at 175.2 and 175.2 ppm) belong to alternating units. In addition, the copolymer composition determined from the relative peak intensities of each monomer unit is in close agreement with the monomer feed amounts used (Table 2).

The experimental molecular weights of P(KLCL) were calculated from ^{13}C NMR data as mentioned earlier. The molecular weight of PCL was calculated from the relative intensity of the carbonyl peak (at 173.5 ppm) of the *N*-acetyl end group (coming from *N*-AcCL initiator) in ratio to the amide carbonyl peak (at 176.0 ppm) of the monomer units. Similarly, the molecular weights of the copolymers were calculated from the relative peak intensities of *N*-acetyl end groups and combined main-chain carbonyl groups corresponding to each monomer unit.

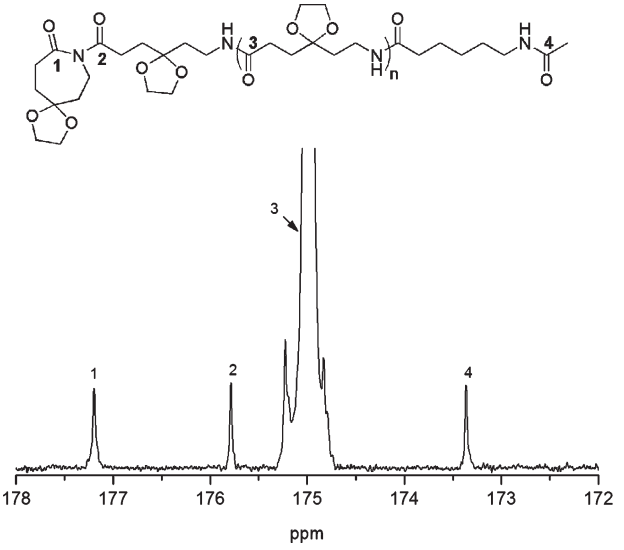


Figure 3. ^{13}C NMR spectrum (carbonyl region only) of P(KLCL) in TFE:$CDCl_3$ solvent mixture.

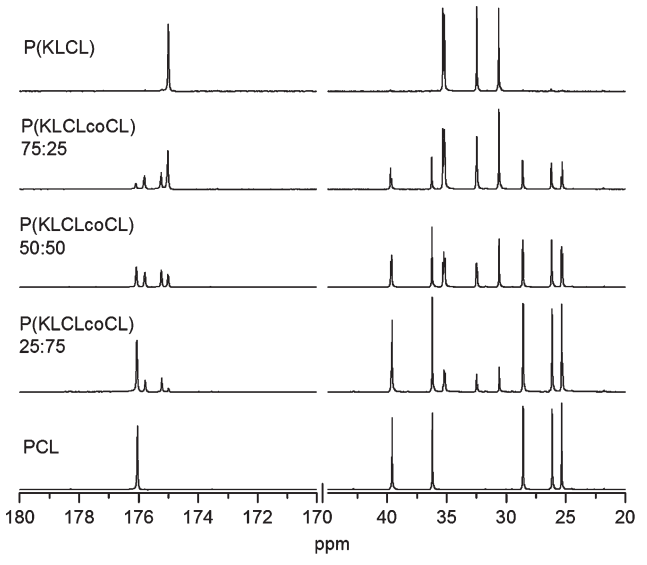


Figure 4. ^{13}C NMR spectra (carbonyl and aliphatic regions) of homo- and copolymers in TFE:$CDCl_3$ solvent mixture.

The synthesis of aliphatic polyamides bearing functional pendant groups is shown in Scheme 2. The first step is the synthesis of polymer bearing ketal pendant groups. Deprotection of the ketone groups was carried out with either aqueous HCl solution or moist trifluoroacetic acid. The ketone groups were then completely reduced to hydroxyl groups using sodium borohydride. Both ^1H and ^{13}C NMR analysis of homopolymers provide clear evidence for the completeness of each reaction step (Figures 5 and 6).

The thermal properties of the polymers and copolymers with ketal, ketone, and hydroxyl pendant groups were analyzed by differential scanning calorimetry (DSC), and the data are summarized in Table 3. On the basis of these results, this new family of polyamides appears to show typical semicrystalline polymer

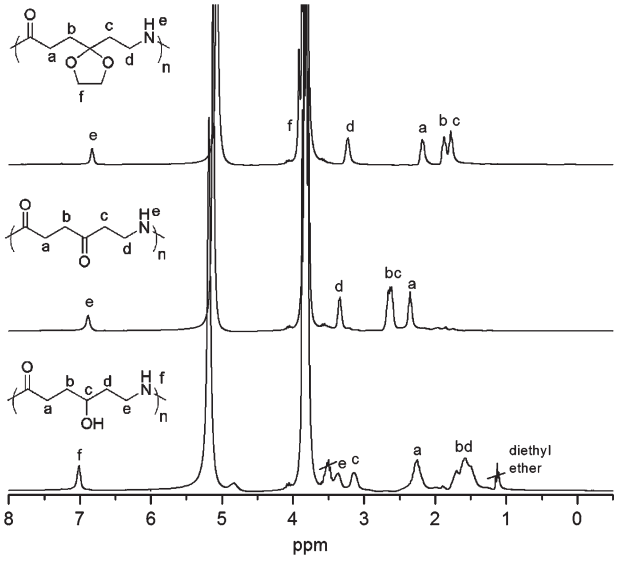


Figure 5. ^1H NMR spectra of P(KLCL), P(KCL), and P(HOCL) in TFE:$CDCl_3$ solvent mixture.

Scheme 2

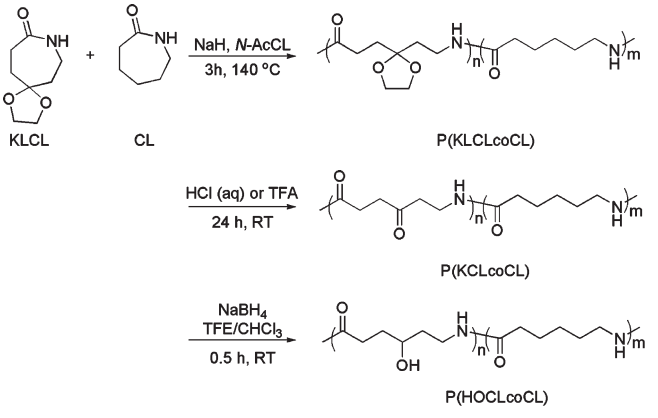


Table 2. Copolymerization of KLCL with CL at Various Molar Compositions (f_{KLCL})

sample	f_{KLCL}[a] (mol %)	conv (%)	F_{KLCL}[b] (mol %)	$M_{n,theo}$[c] (g/mol) ($\times 10^{-3}$)	$M_{n,exp}$[d] (g/mol) ($\times 10^{-3}$)	$[\eta]$[e] (g/dL)	M_v[f] (g/mol) ($\times 10^{-3}$)
P(KLCL)	100	68	100	17.3	16.6	0.55	18.2
P(KLCLcoCL)	75	70	74	15.9	15.7	0.62	20.5
P(KLCLcoCL)	50	88	48	14.4	14.2	0.71	22.9
P(KLCLcoCL)	25	94	24	12.9	12.4	0.91	30.2
PCL	0	99	100	13.3	13.0	1.09	36.1

[a] f_{KLCL}: mol % of KLCL in feed. [b] F_{KLCL}: mol % of KLCL in copolymer. [c] $M_{n,theo}$: molecular weight calculated from monomer-to-initiator ratio. [d] $M_{n,exp}$: molecular weight determined from NMR end-group analysis. [e] $[\eta]$: intrinsic viscosity measured in TFE at 25 °C. [f] M_v: molecular weight calculated from Mark−Houwink equation[8] $[\eta] = 5.36 \times 10^{-4} M^{0.75}$.

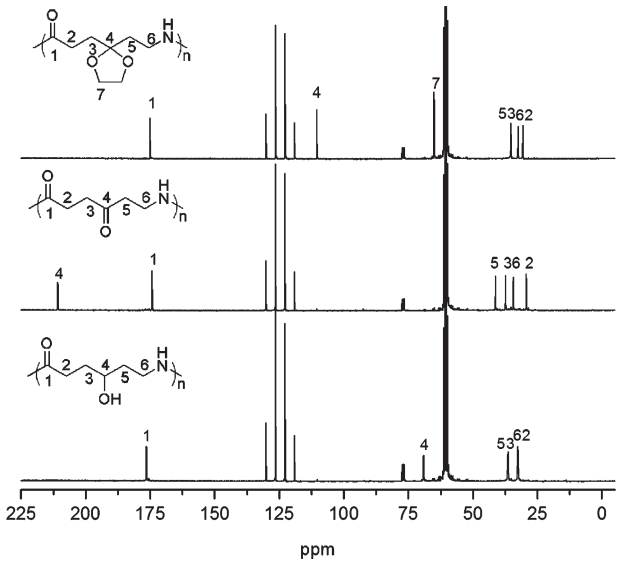


Figure 6. ^{13}C NMR spectra of P(KLCL), P(KCL), and P(HOCL) in TFE:$CDCl_3$ solvent mixture.

Table 3. DSC Data for Homopolymers and Copolymers

sample	comonomer (mol %)[a]	T_m[b] (°C)	ΔH_m (J/g)	T_g[c] (°C)
P(KLCL)	100:0	143	64	60
P(KLCLcoCL)	75:25			55
P(KLCLcoCL)	50:50	123	21	51
P(KLCLcoCL)	25:75	177	69	47
PCL	0:100	222	83	49
P(KCL)	100:0	218	202	158
P(KCLcoCL)	75:25	203	135	127
P(KCLcoCL)	50:50	182	239	81
P(KCLcoCL)	25:75	180	78	51
P(HOCL)	100:0			65
P(HOCLcoCL)	75:25	133	28[d]	57
P(HOCLcoCL)	50:50	162	31	56
P(HOCLcoCL)	25:75	196	51	55

[a] mol % of KLCL in feed. [b] DSC first heating scan. [c] DSC second heating scan. [d] DSC scan after annealing 18 h at 100 °C.

behavior. The glass transition (T_g) values reported here are measured from the second heating scans because in the first scans, very broad transitions were observed which might be caused by the evaporation of residual solvent. T_g values of P(KLCL) as well as its copolymers are higher than the PCL homopolymer. On the other hand, the melting temperatures (T_m) and the melting enthalpies (ΔH_m) of the copolymers are lower compared to those of PCL. This indicates that the rigid ketal groups increase the glass transition temperature while inhibiting close packing and decreasing the melting temperature and crystallinity. T_m values of ketal-containing copolymers also support random copolymer sequences. The melting endotherms of P(KLCL) are only observed in the first DSC scans, and no melting endotherms are observed for the 75 mol % KLCL containing copolymer in the first scan even after annealing at 100 °C for 24 h.

Quite interestingly, after the deprotection of ketone groups, the (co)polymers showed very broad melting endotherms with very high enthalpy values. In fact, the melting enthalpy of the P(KCL) is significantly higher than that of PCL. Even more interesting, while T_g values of the ketal containing (co)polymers are in the range of the values for typical aliphatic polyamides, significantly higher T_g values were observed with increasing comonomer content for the ketone-containing (co)polymers (Table 3). This unexpected increase in the glass transition temperatures of the ketone-containing (co)polymers seemed to indicate that a

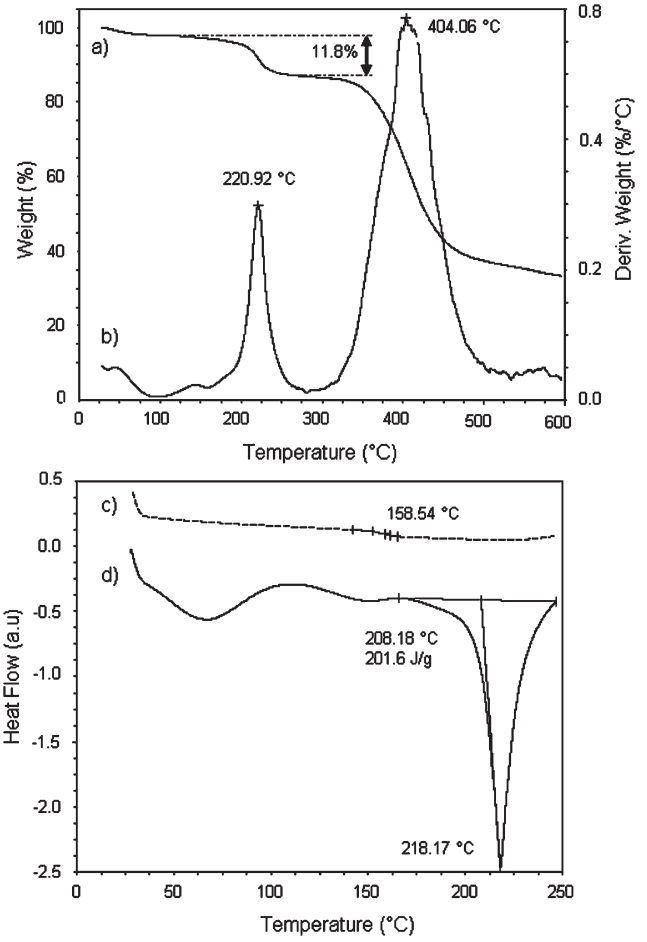


Figure 7. (a and b) TGA and (c and d) DSC thermograms of P(KCL).

thermal cross-linking reaction was taking place. In addition, the high values of melting enthalpies might be explained by assuming that the cross-linking reaction is endothermic. In order to shed more light on this unexpected thermal behavior, a series of experiments were carried out.

First, the melting behavior of the ketone-containing homopolymer, P(KCL), was observed visually using a capillary melting apparatus. As soon as polymer started to melt, the color turned pale yellow and extensive bubble formation took place, consistent with some form of reaction occurring. Second, the films of homopolymer and copolymers were prepared by melt pressing. The pressed films were yellow in color and contained trapped bubbles inside. More importantly, they totally lost solubility in the solvents which can dissolve the polymers before melt pressing. This behavior was observed even at very low comonomer content, i.e., 5 mol %.

Further analysis by TGA revealed a two-stage thermal decomposition process (Figure 7a). The temperature at which the greatest weight loss was observed in the first stage before decomposition (derivative temperature curve, Figure 7b) is very close to the melting temperature observed in the DSC first heating scan (Figure 7d). This clearly indicates that a reaction liberating a volatile compound is taking place soon after melting starts. In addition, the residual wt % at 600 °C is above 30%, consistent with cross-linking which facilitates char formation. The TGA curves of ketone-containing copolymers (data not shown) also show two-stage thermal decomposition, and the percentage of residue at 600 °C increased with ketone comonomer content.

The change in the chemical structure upon heating above the melting temperature of the polymer could not be investigated by solution NMR analysis because the polymers became insoluble.

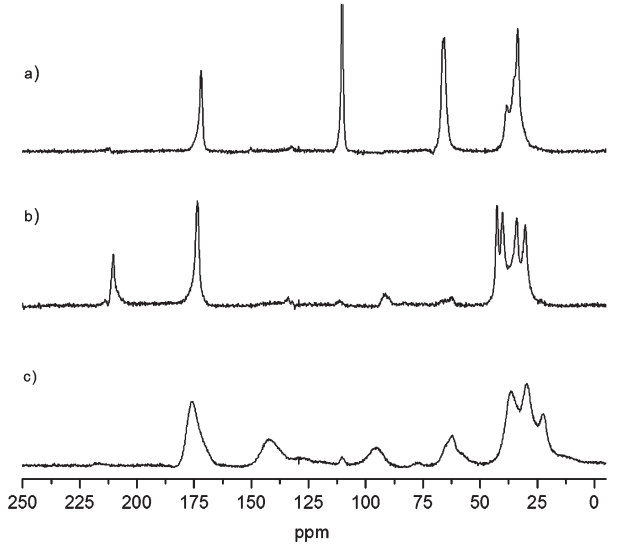


Figure 8. ^{13}C TOSS spectra of (a) P(KLCL), (b) P(KCL), and (c) P(KCL) after melting.

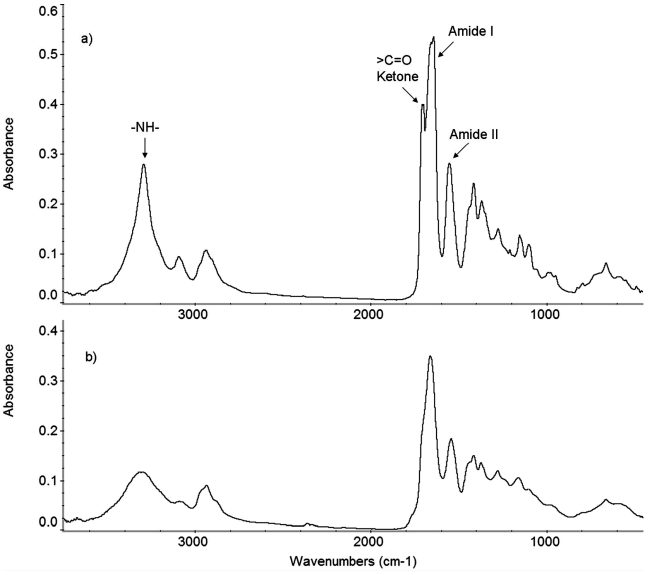
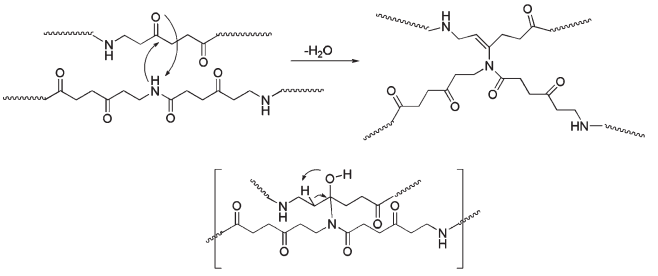


Figure 9. FTIR spectra of P(KCL) (a) before UV irradiation and (b) after 5 h UV irradiation.

Scheme 3



Fortunately, solid-state NMR experiments enabled monitoring of the change in chemical composition. As it can be seen in Figure 8b,c, the ketone group at 205 ppm completely disappeared upon heating the polymer above its melting temperature, and new peaks formed at ca. 142 and 97 ppm. There is also an obvious change in the aliphatic region, consistent with the number of methylene groups decreasing from four to three after cross-linking. In addition to NMR, FT-IR analysis of the melt-pressed films (data not shown) showed significant reduction of amide and ketone group absorptions, indicative of reaction between ketone and amide groups after heating and two new peaks appeared at 1332 and 1204 cm^{-1}.

Thermal properties of polyamides bearing ketone groups were analyzed previously by Pearce et al.[13] The carbonyl groups were introduced into the backbone by the interfacial polymerization of ketone containing diacid chlorides and diamines. Similar to our results, they obtained insoluble materials when the polymer samples were heated above 300 °C. FT-IR analysis of their heated samples showed reduction of the peak intensities of both ketone and amide groups. According to our visual observations and spectroscopic analysis, as well as this support from the literature,[13] the most reasonable cross-linking mechanism suggested involves the attack of amide nitrogen at the ketone carbonyl with subsequent loss of water and formation of enamide linkages between chains (Scheme 3). Although solid-state NMR data for enamides could not be found in the literature, the peaks at 142 and 97 ppm in the TOSS spectrum of P(KCL) after cross-linking (Figure 8c) are in close agreement with chemical shifts in solution NMR spectra of enamides.[14] Furthermore, assuming water is the product of this reaction and all or most of the ketone groups are consumed, the calculated weight loss is 13.8% while the actual value determined from TGA (Figure 7a) is in close agreement at 11.8%.

The ketone-containing polymers are sensitive to not only thermal cross-linking but also photo-cross-linking. The thin films of P(KCL) were irradiated as described in the Experimental Section. The FT-IR spectra of a polymer film before and after 5 h irradiation are given in Figure 9. The most distinguishable changes are due to reduction in the peak intensity for both ketone groups (1700 cm^{-1}) and amide groups (1645 and 1555 cm^{-1}), especially the NH stretching at 3300 cm^{-1}. However, the reduction in the peak intensities was not as significant as in the melt-pressed films. The FT-IR photodegradation studies of previously investigated ketone-containing AA−BB type nylons showed similar results.[15] In addition to FT-IR analysis, we observed that the films became insoluble after photolysis, consistent with a photo-cross-linking mechanism that involves reaction of both ketone and amide groups.

Reductive conversion of the ketone groups to hydroxyls results in decreases in T_m and melting enthalpies compared to ketal containing homo- and copolymers and PCL homopolymer (Table 3). In fact, a melting endotherm of P(HOCL) which was previously precipitated from TFE solution into diethyl ether was not observed for either first or second scans. In addition, the copolymers containing 75 mol % HOCL did not show any melting endotherm in the second scan, and virtually no change in T_g was observed. The hydroxyl-containing homopolymer was also soluble in water and methanol at room temperature. These results are consistent with the hydroxyl groups disrupting packing and reducing overall crystallinity in the homo- and copolymers.

Conclusions

The synthesis of 5-azepane-2-one ethylene ketal from 1,4-cyclohexandione monoethylene ketal was accomplished using an efficient and high yielding procedure under very mild conditions. It homo- and copolymerized efficiently using anionic ring-opening methods. The deprotection of the polymer chains quantitatively released ketone groups which then could be reduced to hydroxyl pendant groups. The ketone-containing polymers respond sensitively to both thermal and photo-cross-linking conditions for this novel class of materials. Indeed, after cross-linking, solubility in organic solvents is lost, and

increasingly high glass transition temperatures are obtained with increasing KCL content. The sensitivity to thermal and photo-cross-linking is a special feature of the ketone-containing polymers. In other words, the ketal- and hydroxyl-containing polymers do not undergo cross-linking upon heating or UV irradiation. Thus, aliphatic polyamides bearing ketone and hydroxyl pendant groups can be easily prepared and provide pathways to new applications in a broad variety of uses.

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