Poly(2-oxepane-1,5-dione): A Highly Crystalline Modified Poly(ϵ-caprolactone) of a High Melting Temperature

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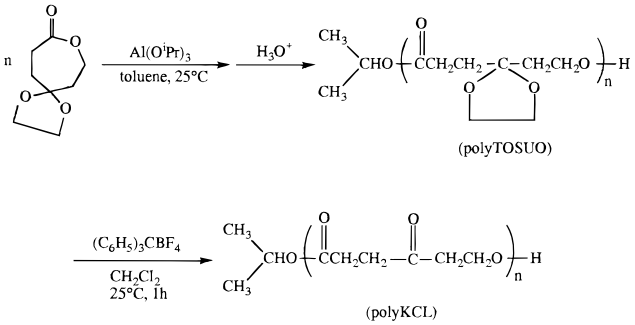
Steadily increasing attention has been paid to biodegradable polymers not only for their potential in agricultural and medical fields but also for the waste management of plastics. The field of biodegradable polymers is however very much materials-limited.[1,2] Poly(ϵ-caprolactone) (PCL) is one of the very few commercially available biodegradable polymers. It is well-known for a unique set of properties, which includes biocompatibility, permeability, and biodegradability.[3] The range of these properties is furthermore increased by copolymerization with lactides and glycolide, which accounts for widespread applications in medicine as biodegradable sutures, artificial skin, resorbable prostheses and containers for sustained drug release.[3−7] In addition to biodegradability and biocompatibility, PCL has also the rarely met property of being miscible with a variety of polymers, e.g. Bisphenol A polycarbonate and PVC, which allows some deficient properties of these polymers to be improved, such as poor stress−crack resistance and lack of gloss and adhesion.[8,9] Furthermore, when deficient properties are concerned, a too low melting temperature (ca. 60 °C) is a severe limitation to PCL applications. When waste plastics, even those known for biodegradability, are disposed of by burying them in landfills, it is not unusual that they remain untouched and entombed indefinitely.[1] Therefore, developing polymers that are photodegradable is an attractive alternative for intrinsically biodegradable polymers. It is worth recalling that only a small portion of the sun energy reaches the earth's surface; namely, rays with a wavelength higher than 290 nm can break single covalent bonds (165−420 kJ/mol). Most organic synthetic polymers that contain C−C, C−H, C−O, C−N, and C−Cl bonds do not absorb at wavelengths longer than 190 nm, and thus remain unaffected by sunlight. Only when polymers contain chromophores, such as ketones, can they absorb radiations in the 200−400 nm range and radiation of even longer wavelengths.[10,11]

This paper aims at reporting on an efficient route to novel aliphatic polyesters that have the structure of poly(ϵ-caprolactone) but are modified by one ketone function per monomer unit. Compared to unmodified PCL, this polyester is highly crystalline, has a much higher melting temperature, and has the potential of being photodegradable. Scheme 1 shows the synthetic pathway of this novel aliphatic polyester.

Scheme 1. Synthetic Pathway to Poly(5-ketone ϵ-caprolactone)



1,4,8-Trioxaspiro[4.6]-9-undecanone (TOSUO) has been prepared as described elsewhere[12] and was polymerized in toluene at 25 °C by using aluminum isopropoxide ($Al(O^iPr)_3$) as an initiator. Polymerization conditions and polymer characteristics are listed in Table 1. As reported elsewhere, this homopolymerization is living and first order with respect to both the monomer and the initiator.[13] The polymerization mechanism is consistent with the coordination of $Al(O^iPr)_3$ to the exocyclic carbonyl oxygen of TOSUO, followed by the acyl−oxygen cleavage of the monomer and insertion into the Al−O bond of the initiator. This mechanism accounts for an isopropyl ester end-group (a multiplet at 5.01 ppm (H_b) and a doublet at 1.24ppm (H_a) in a 1:6 ratio, Figure 1A) and a hydroxyl end-group formed as result of the hydrolysis of the propagating aluminum alkoxide. The methylene protons (H_f) of the CH_2OH end-group is observed as a triplet at 3.75 ppm and its relative intensity with respect to the H_a and H_b protons confirms that there are as many isopropylester end-groups as hydroxyl ones. Three polyTOSUO samples of a different molecular weight (M_n = 5000, 15 000, 26 000) have been synthesized (Table 1), whose the molecular weight distribution is symmetrical and narrow (1.2) as confirmed by size-exclusion chromatography.

Triphenylcarbenium tetrafluoroborate has proved to be a useful and efficient reagent for the deacetalization of the ketone acetal group of polyTOSUO.[12,15] This deacetalization reaction is complete, even for the sample of the highest molecular weight (26 000). Indeed, the ^{1}H-NMR spectrum for poly(2-oxepane-1,5-dione) (Figure 1B) shows that the acetal protons at δ = 3.94 ppm have completely disappeared, whereas the multiplets at δ = 1.98 ppm (H_{d1+d2}) and triplets at δ = 2.36 (H_c), 4.16 (H_e), and 3.75 ppm (H_f), respectively, of the original polyTOSUO (Figure 1A) have accordingly been shifted to lower fields (δ = 2.91 ($H_{d1'+d2'}$), 2.66 ($H_{c'}$), 4.40 ($H_{e'}$) and 3.92 ppm ($H_{f''}$)). This novel aliphatic polyester, poly(γ-ketone ϵ-caprolactone) (polyKCL), is not soluble in common solvents such as $CHCl_3$, acetone, THF, toluene, DMSO, etc., even at high temperature. It is soluble in trifluoroacetic acid (TFAA) and in a solvent mixture of TFAA with $CDCl_3$ (1:5 v:v), in which the ^{1}H-NMR spectrum has been recorded.

The thermal properties of poly(2-oxepane-1,5-dione), polyTOSUO and PCL have been analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). All the thermal properties are listed in Table 2, and a typical DSC thermogram is shown in

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Table 1. Homopolymerization of TOSUO initiated by Al(O^{i}Pr)$_3$ in toluene at 25 °C

samples	$[M]_0/[I]_0$	M_n[a] (theor)	polymzn time (h)	% conversion	M_n[b] (exptl)	M_n[c] (SEC)	M_w/M_n
PTOSUO1	29.0	5.0K	5	100	5.1K	2.5K	1.20
PTOSUO2	87.1	15.0K	12	100	15.4K	7.0K	1.20
PTOSUO3	174.3	30.0K	16	87	26.0K	8K	1.20

[a] M_n(theor): theoretical molecular weight; K stands for thousand. [b] M_n(exptl): experimental molecular weight as determined by ^{1}H NMR from the relative intensity of protons H_a and H_c in Figure 1. [c] M_n(SEC) based on polystyrene standards with the universal calibration for PCL.[14]

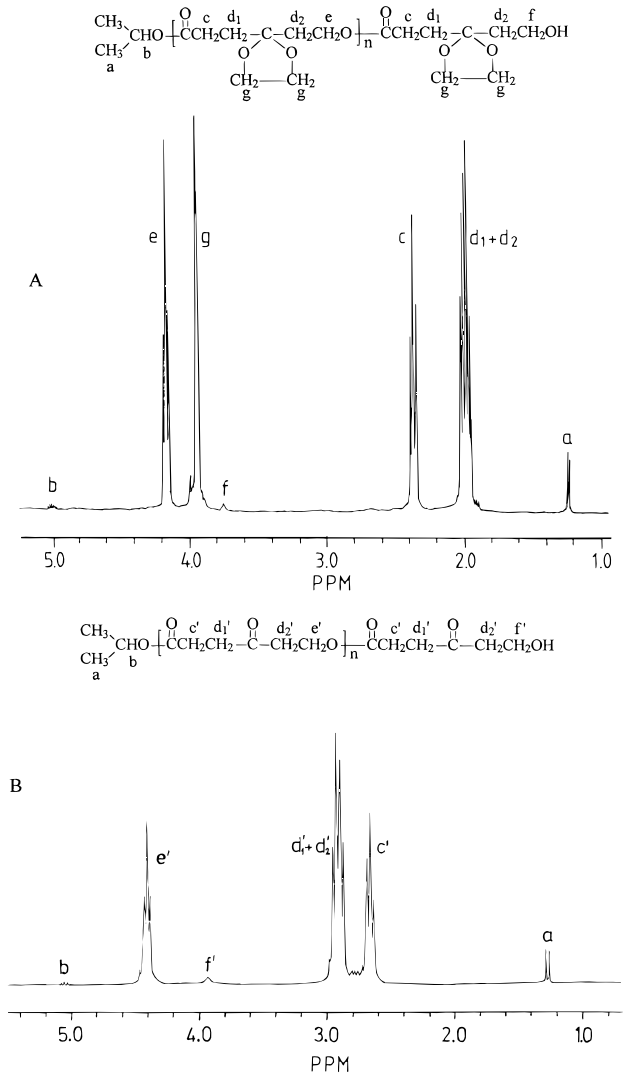


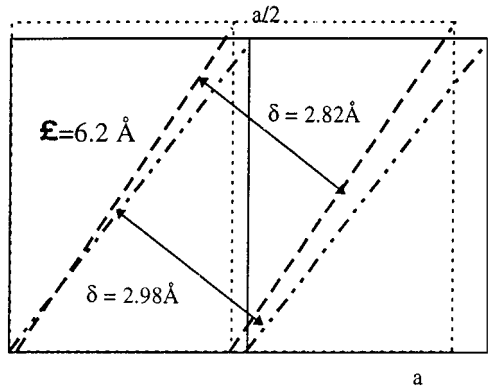
Figure 1. ^{1}H-NMR spectra of polyTOSUO (M_n = 5 K) before deacetalization in $CDCl_3$ (A), and after deacetalization (polyKCL) in TFAA/$CDCl_3$ (1:5 volume ratio) (B).

Table 2. DSC and TGA Data for PCL, PolyTOSUO, and PolyKCL

samples	M_n ($\times 10^{-3}$)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_d (°C)
PCL	15.0	−61	59	85.0	399
PTOSUO	15.5	−16	52	35.0	279
PKCL	3.8	41	141	112.7	221
PKCL	11.5	41	149	107.4	227
PKCL	19.5	41	153	100.4	224

Figure 2. The glass transition temperature (T_g) of polyTOSUO is ca. 45 °C higher than T_g of PCL, but its melting temperature (T_m) and melting enthalpy (ΔH_m) are smaller compared with those for PCL. Interestingly enough, T_g, T_m, and ΔH_m of polyKCL are much higher than those for the parent PCL (by 100 °C for T_g, by 90 °C for T_m, and by 25 J/g for ΔH_m). This substantial

Scheme 2



improvement, particularly in T_m, is now able to overcome the severe limitation which is commonly placed on the PCL applications. Although the melting temperature of polyKCL increases with molecular weight, the glass transition temperature of this highly crystalline polyester is essentially independent of it. According to thermogravimetric analysis, PCL, polyTOSUO, and polyKCL ($M_n \approx$ 15K) experience a sharp thermal decomposition under nitrogen at 399, 279, and 227 °C, respectively, so that thermal stability increases as follows: PKCL < PTOSUO < PCL.

The WAXS pattern of polyKCL shows three major peaks at Bragg spacings of 4.08, 3.375, and 2.82 Å, respectively, whose relative intensities decrease as 100, 40, and 10.

A similar pattern was reported for PCL with Bragg spacings at 4.15, 3.73, and 2.97 Å, and with the same intensity ratios. According to Chatani et al. the crystal structure of PCL is in the space group $P2_12_12_1$, with the unit cell axes a = 7.49 Å, b = 4.98 Å, and c = 17.03 Å, two molecules being extended along the c axis.[16] The molecules are planar and the plane of the molecule is approximately parallel to the diagonal of the half-cell defined by the b-axis and $a/2$ (Scheme 2). So, the extent of the molecule in its plane is given by £ = $(b^2 + a^2/4)^{1/2}$. The distance between two neighbor molecules is $\delta = ab/2£$ with £ = 6.2 Å. The distance δ is actually the (210) Bragg spacing equal to 2.98 Å for PCL.

Where polyKCL is concerned, the corresponding δ peak must be one of the two peaks observed at 3.375 and 2.82 Å. On the basis of this hypothesis and the value of £ found for PCL (6.2 Å), the a and b axes can be approximated. In case of δ = 2.82 Å, the following set of values is found: a = 6.69 Å and b = 5.25 Å. No solution emerges in case of δ = 3.375 Å. Then, the powder pattern of polyKCL has been indexed by taking into account the systematic extinctions of the $P2_12_12_1$ space group (h00, 0k0, 00l, with odd h, k, or l). Data are reported in Table 3, and the axes have been calculated as $a = 6.80 \pm 0.03$ Å, $b = 5.18 \pm 0.03$ Å, and $c = 17.17 \pm 0.09$ Å. The agreement is acceptable within the limits of the assumptions and considering the poor

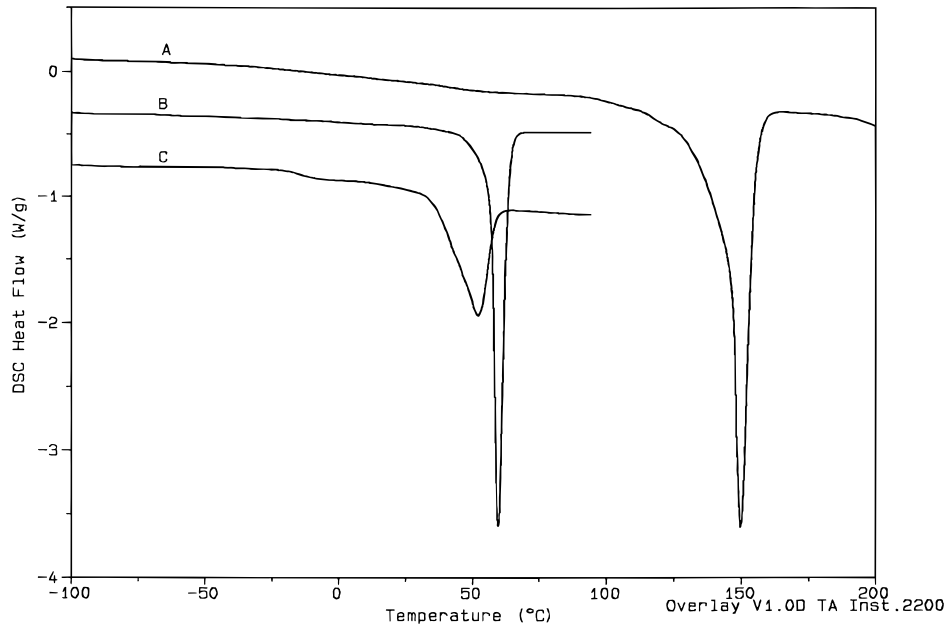


Figure 2. DSC thermogram (first scan) of (A) polyKCL (M_n = 11.5 K), (B) PCL (M_n = 15 K), and (C) polyTOSUO (M_n = 15.5 K).

Table 3. Comparison of the Observed and Calculated Structure Factors for PolyKCL

d_{obs}	hkl	d_{calc}
6.272	101	6.329
4.783	011	4.957
4.080	110	4.121
3.375	200	3.404
3.968	111	4.007
2.820	210	2.844
2.820	006	2.861
2.610	106	2.638
2.610	115	2.638
2.549	020	2.589
2.549	213	2.547
2.344	116	2.350
2.211	024	2.217
2.211	123	2.229
2.070	220	2.061
2.070	310	2.079
2.040	108	2.047
1.685	321	1.698
1.656	402	1.670

crystallinity of the polymeric sample. There is thus an increase in the *b*-axis and a significant decrease in the *a*-axis with respect to the PCL cell. Assuming that the molecule plane is parallel to the *c*-axis and to the diagonal of the half cell (*b*, *a*/2) and that the extent of the molecule in its plane is 6.2 Å, as is the case for PCL, the distance between two neighbor molecules then decreases from 2.98 Å in PCL to 2.82 Å in polyKCL. This modification indicates that the strength of the intermolecular interactions is higher in polyKCL, consistently with the observed increase in the melting temperature from 60 °C for PCL to 150 °C for polyKCL.

In nature, photodegradable polymers are degraded by chain scissions promoted by the sunlight and usually oxygen, yielding low molecular weight material.[17] Since only absorption at and above 290 nm can cause photochemical modifications, the UV absorption spectrum of a polymer is of a critical importance when photosensitivity is concerned. Ketone usually shows an absorption band with a maximum at 270−290 nm, that extends into the region above 300 nm. This absorption is a n−π* transition,[18] which involves the excitation of an electron from a nonbonding n orbital localized on the oxygen atom to a more delocalized antibonding π* orbital distributed over the entire carbonyl group. Figure 3 shows the UV absorption spectra of PCL and polyKCL. The absorption band of PCL is quite narrow, centered at 240 nm and assigned to the carbonyl of the ester groups. The absorption band of polyKCL is very broad with a maximum at 270 nm and an absorption tails extending beyond 300 nm, which is the signature of the ketone groups in addition to the ester ones. The maximum of the absorption band shown by PCL is shifted to 252 nm in case of polyKCL. By reference to the well-established photodegradation mechanism of polymers containing ketone groups,[19−22] the novel aliphatic polyester, polyKCL, has not only a great similarity to PCL but also more importantly a much higher melting temperature and the structural characteristics of a photodegradable polymer.

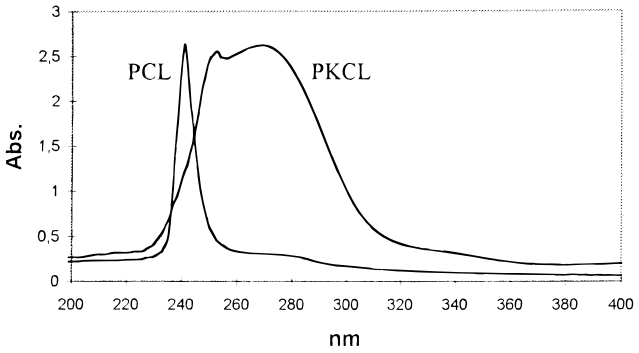


Figure 3. UV absorption spectra of PCL and polyKCL.

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References and Notes

(1) Lenz, R. W. Biodegradable Polymers. *Adv. Polym. Sci.* **1993**, *107*, 3.

(2) Lenz, R. W. Design, Synthesis and Applications of Biodegradable Polymers In *International Symposium on Biodegradable Materials, Hamburg (Germany),* Oct. 1996.
(3) Pitt, C. G.; Marks, T. A.; Schindler, A. Biodegradable Drug Delivery Systems based on Aliphatic Polyesters: Application of Contraceptives and Narcotic Antagonists. In *Controlled Release of Bioactive Materials*; Baker, R., Ed.; Academic Press: New York, 1980.
(4) Schindler, A.; Jeffcoat, R.; Kimmel, G. L.; Pitt, C. G.; Wall, M. E.; Zweidinger R. Biodegradable Polymer for Sustained Drug Delivery In *Contemporary Topics in Polymer Science*; Pearce, J. R., Schaefger, E. M., Eds.; Plenum: New York, 1977; Vol. 2, p 251.
(5) Vert, M. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 109.
(6) Pak, J.; Ford, J. L.; Rostron, C.; Walters, V. *Pharm. Acta Helv.* **1985**, *60* (5), 160.
(7) Grijpma, D. W.; Zondervan, G. J.; Pennings A. J. *Polym. Bull.* **1991**, *25*, 327.
(8) Brode, C. L.; Koleske, J. V. *J. Macromol. Sci.-Chem.* **1972**, *A6*, 1109.
(9) Olabisi, O.; Robeson, L. E.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic: New York, 1979.
(10) Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*; Elsevier Scientific Publishing Company: Amsterdam, Oxford, England, and New York, 1976.
(11) Rabek, J. F. *Experimental Methods in Polymer Chemistry: Physical Principles and Applications*; John Wiley & Sons: New York, 1982.
(12) Tian, D.; Dubois, Ph.; Grandfils, Ch.; Jérôme, R. *Macromolecules* **1997**, *30*, 406.
(13) Tian, D.; Dubois, Ph.; Jérôme, R. *Macromolecules* **1997**, *30*, 1947.
(14) Heuschen, J.; Jérôme, R.; Teyssie, Ph. *Macromolecules* **1981**, *14*, 242.
(15) Barton, D. H. R.; Magnus, P. D.; Smith, G.; Zurr, D. *J. Chem. Soc., Chem. Commun.* **1971**, 861.
(16) Chatani, Y.; Okita, Y; Tadokoro, H.; Yamashita, Y. *Polym. J.* **1970**, *1*, 555.
(17) Swift, G. Polymer, Environmentally Degradable. In *Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Ed.; John Wiley & Sons: New York, 1996; Vol. 19, p 968.
(18) Pitts, J. N.; Wilkinson, F., Jr.; Hammond, G. S. *Adv. Photochem.* **1963**, *1*, 1.
(19) Bamford, C. H.; Norrish, R. G. W. *J. Chem. Soc.* **1935**, 1504.
(20) McMillan, G. R.; Calvert, J. G.; Pitts, J. N. *J. Am. Chem. Soc.* **1964**, *86*, 3602.
(21) Hartley, G. H.; Guillet, J. E. *Macromolecules* **1968**, *1*, 165.
(22) Amerik, Y.; Guillet, J. E. *Macromolecules* **1971**, *4*, 375.

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