Macromolecules 1987, *20*, 1199–1204

structure should be highly trans in its 1,4 component, as was observed, 84% trans independent of temperature.[12]

Curvature in the Arrhenius plot of rates of butadiene polymerization with sodium as counterion in THF can be interpreted[11] as indicating that the cis,trans population is close to equilibrium at 0 °C and above but out of equilibrium increasingly at lower temperatures. This was at the same time confirmed by observations of the near-UV spectra of the active centers. According to the present results, even at 0 °C equilibration may not be complete at $[M]_0 = 0.2$ M since both the average active center lifetime and the isomerization half-life are about 8 s. Extrapolation errors in k_{tc}, however, introduce some degree of uncertainty in this conclusion. By −30 °C, however, direct measurements are available for both rates. Equilibration of active center isomers is impossible at this temperature, for the isomerization half-life is about $4^1/_2$ min whereas the average active center lifetime is 1–20 s in a normal monomer concentration range. It is not surprising therefore that the 1,4 units in the polymer were found to be virtually all trans in structure at −78 °C with Na^+ as counterion.

In butadiene polymerization with lithium as counterion in THF, trans,cis equilibration is much faster and monomer addition rates slower than with the other counterions. Extrapolation of isomerization rates to 0 °C is sufficiently accurate to give a reasonable estimate of the isomerization half-life as ~0.2 s. At an initial monomer concentration of 0.2 M, the average active center lifetime is 83 s (or 17 s at 1 M monomer). Equilibration will be possible generally at this temperature. At −78 °C the isomerization half-life approaches 1 h. Polymerization rates are very low at this temperature and not measurable with high accuracy. Monomer half-lives will be on the order of several tens of hours at initiator concentrations of 10^{-3}–10^{-2} M. At a conventional range of monomer concentrations (0.2–2 M), the polymerization process appears to be at the critical point where monomer concentration is important. The mean active center lifetime at an average monomer concentration of ~0.7 M was found to be ~0.9 h ($k_p \sim 4 \times 10^{-4}$ M^{-1} s^{-1}), i.e., comparable to the isomerization half-life. The trans content in the 1,4 in-chain structures was, however, already ~90%. These results again are only consistent with a greater reactivity of trans forms.

The measurements of isomerization rates, therefore, confirm generally the scheme suggested previously[9,11] based principally on spectroscopic and polymerization rate data where the sodium counterion was used.

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Synthesis of Polyesters Having Pendant Ester Groups by Ring-Opening Polymerization of 4-Methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one

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ABSTRACT: A new polyester (**6**) having tetrahydropyran rings in the backbone chain and methoxycarbonyl groups as side chains was synthesized by the ring-opening polymerization of 4-methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one (**5**). Monomer **5** was prepared from acrolein and dimethyl malonate via five reaction steps in an overall yield of 23%. Polymerization of **5** was carried out in dichloromethane at −90, −60, and −30 °C with the use of Lewis acid initiators. Soluble polymers having molecular weights up to 1.5×10^5 were obtained with boron trifluoride etherate, whereas a cross-linked polymer was formed with phosphorus pentafluoride. Polyester **6** was soluble in a variety of solvents including chloroform, γ-butyrolactone, acetone, acetonitrile, and dimethyl sulfoxide. It gradually decomposed at 142–152 °C. Copolymerization of **5** with its parent compound 2,6-dioxabicyclo[2.2.2]octan-3-one (**1**) has revealed that the introduction of a methoxycarbonyl group at the 4-position markedly reduces the polymerizability of the lactone ring. The hydrolysis of films of polyester **6** was examined in 0.001 N hydrochloric acid at 60 °C and compared with that for structurally relevant polyesters **2** and **4**.

Introduction

A variety of biologically and biomedically important polymers possessing well-defined heterocyclic structures in their backbones have been produced by ring-opening polymerization of heterobicyclic compounds such as bicyclic acetals, lactones, and lactams.[1-5] Very recently, we synthesized new polyesters **2** and **4** containing tetrahydropyran rings in their main chains by the cationic and

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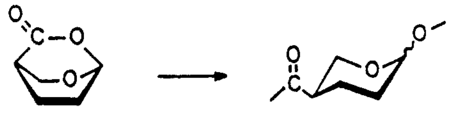
Table I
Homopolymerization of 4-Methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one (5)[a]

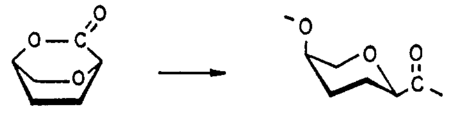
solv, mL	init	amt init, mol %	temp, °C	time, h	yield,[b] %	$M_n{}^{b,c} \times 10^{-4}$	$M_w/M_n{}^{b,c}$	cis:trans[d]
4.5	PF_5	3	−60	1	65[e]			34:66
4.5	BF_3OEt_2	2	−30	1	75	6.1	1.6	41:59
4.5	BF_3OEt_2	5	−60	1	76	2.1	1.7	34:66
4.5	BF_3OEt_2	2	−60	1	73	5.6	1.7	37:63
7.0	BF_3OEt_2	2	−90	17	71	15	2.2	22:78

[a] Monomer, 3 mmol; solvent, dichloromethane. [b] Methanol-insoluble polymer. [c] By gel permeation chromatography (polystyrene standard). [d] By ^{1}H NMR spectroscopy. [e] Swollen in chloroform.

anionic ring-opening polymerization of two bicyclic oxalactones, 2,6-dioxabicyclo[2.2.2]octan-3-one (1) and 2,5-dioxabicyclo[2.2.2]octan-3-one (3), respectively.[6,7]



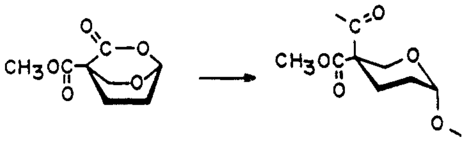
1 2



3 4

The presence of six-membered rings in the main chain generally imparts desirable physical properties to the polymer, including high crystallinity, thermal stability, and excellent mechanical properties such as tenacity and modulus. In fact, polyester 4 derived from 3 was a crystalline polymer exclusively consisting of cis-2,5-linked tetrahydropyran units and had a high melting point of 290 °C for a molecular weight of 1.4 × 10^4.[7] On the other hand, 1 readily underwent cationic polymerization at low temperature to polyester 2, having a molecular weight up to 1.1 × 10^5. Polyester 2 could be cast into a flexible transparent film.[6] However, the film disintegrated after it had been immersed in water for a period of several weeks. This finding, along with a preliminary test showing that polyester 2 is capable of forming fibrous material, suggests that polyester 2 may be a promising candidate for biomedical application, in particular for biodegradable surgical sutures and for encapsulation of drugs.

As an extension of a series of studies on the synthesis of oxacyclic polymers of potential biomedical utility, we describe herein synthesis of a new bicyclic oxalactone 4-methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one (5) and its cationic homopolymerization and copolymerization with the parent compound 1 to polyesters 6 having pendant ester groups. The present work aims at clarifying the effects of the ester group on the polymerizability of bicyclic lactones on the one hand and on the physical and chemical properties of polyesters having tetrahydropyran rings in the backbone chains on the other hand.

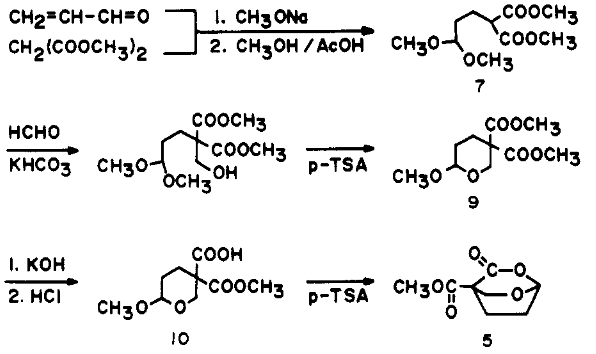


5 6

Results and Discussion

Synthesis of Monomer. 4-Methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one (5) was synthesized from acrolein and dimethyl malonate in a manner similar to the synthesis of its parent compound 1.[6] Scheme I illustrates the synthetic route for the bicyclic oxalactone 5.

Scheme I
Synthetic Route for
4-Methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one (5)



The synthesis of the intermediate dimethyl 6-methoxytetrahydropyran-3,3-dicarboxylate (9) from the starting materials has been described previously.[6] The diester 9 was saponified in methanol with an equimolar amount of aqueous sodium hydroxide followed by neutralization with hydrochloric acid to give methyl hydrogen 6-methoxytetrahydropyran-3,3-dicarboxylate (10). The half-ester 10 was heated in a dilute toluene solution in the presence of a small amount of *p*-toluenesulfonic acid to yield the bicyclic lactone 5. The acid-catalyzed intramolecular cyclization was effectively achieved by continuously removing liberated methanol through a Soxhlet extractor containing molecular sieves 4A. Repeated recrystallization from diethyl ether gave 5 as colorless crystals. The overall yield of 5 on the basis of acrolein was approximately 23%. The bicyclic lactone 5 formed hygroscopic crystals melting at 93–94 °C. The DSC thermogram showed that an endothermic peak appeared at 86–88 °C followed by an exothermic peak at 89 °C before an endothermic peak due to melting appeared at 93–94 °C. The thermal behavior is probably ascribable to the transformation of crystalline forms.

Polymerization. Cationic homopolymerization of 5 was carried out in dichloromethane at −90, −60, and −30 °C. Boron trifluoride etherate and phosphorus pentafluoride were used as initiators. Some of the results are summarized in Table I.

Completely soluble polymers were obtained with boron trifluoride etherate as the initiator, whereas an insoluble polymer only swelling in chloroform was produced with phosphorus pentafluoride, presumably by cross-linking reactions involving pendant ester groups. The polymers obtained with boron trifluoride etherate were soluble in a variety of solvents including chloroform, dichloromethane, γ-butyrolactone, pyridine, tetrahydrofuran, acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide. Since polyester 2 was soluble in the former four solvents only, the solubility was markedly improved by the introduction of the pendant methoxycarbonyl groups. The

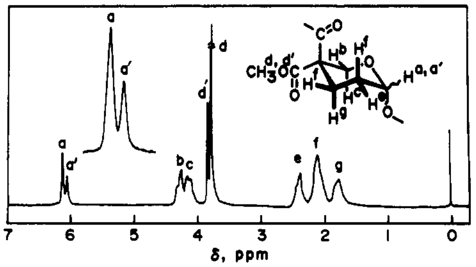


Figure 1. ^1H NMR spectrum of poly[(5-(methoxycarbonyl)-tetrahydropyran-5,2-diyl)oxycarbonyl] (6) prepared at −60 °C with boron trifluoride etherate as initiator: solvent, $CDCl_3$; temperature, 50 °C; internal reference, tetramethylsilane; 200 MHz.

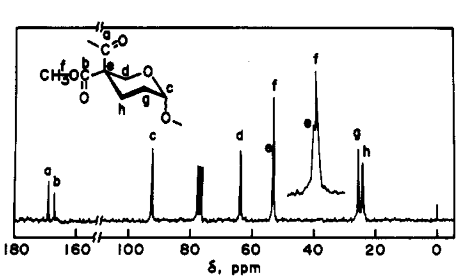
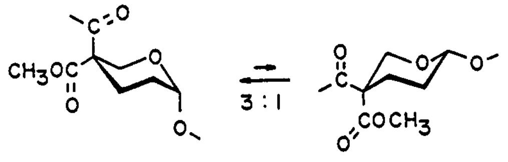


Figure 2. ^{13}C NMR spectrum of poly[(5-(methoxycarbonyl)-tetrahydropyran-5,2-diyl)oxycarbonyl] prepared at −60 °C with boron trifluoride etherate as initiator: solvent, $CDCl_3$; temperature, 50 °C; internal reference, tetramethylsilane; 50 MHz.

molecular weights of the polymers determined by gel permeation chromatography ranged from 2.1 × 10^4 to 15 × 10^4 (polystyrene standard). These polymers gradually decomposed at 142–152 °C (DSC). Methyl hydrogen 3,4-dihydro-2*H*-pyran-3,3-dicarboxylate and bicyclic lactone **5** were identified as the chief decomposition products. A transparent flexible film could be cast from a chloroform solution of the high molecular weight polymer. After the film was immersed in water for 48 h, its water content was 2.8% by weight, somewhat higher than that for polyester **2** (1.7% by weight).

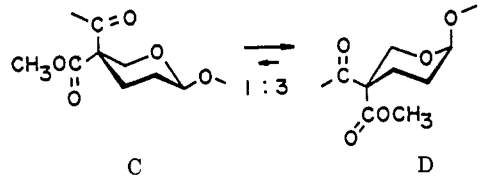
Structure and Stereochemistry. As **5** can be regarded as an acetal ester, it is anticipated that its C(1)–O(2) bond is preferentially cleaved in the cationic ring-opening polymerization. In fact this was proved in the polymerization of the parent compound **1**, where polyester **2** containing both cis- and trans-2,5-linked tetrahydropyran rings was produced.

Figure 1 presents the ^1H NMR spectrum of the polymer prepared at −60 °C with boron trifluoride etherate as the initiator. The signals were assigned as indicated in Figure 1. It is noteworthy that the signals assignable to the methine proton on C(1) (anomeric proton) and the methoxy protons appear as a pair of peaks with different intensities (δ 6.08 and 6.02 for the former, and δ 3.82 and 3.76 for the latter). This is undoubtedly indicative of the presence of structurally different units in the polymer chain, that is, trans- and cis-2,5-linked tetrahydropyran units. (Hereafter these units are referred to as trans and cis units, respectively.)



A B

trans unit



C D

cis unit

Both the trans and cis units are in conformational equilibrium with their flipped structures. The free energy differences between the conformers were estimated to be 2.5 kJ/mol in favor of conformers A and D by using the following numerical parameters of substituents in tetrahydropyrans (kJ/mol):[8] 6-$OCOCH_3$, −2.5;[9] 3-$COOCH_3$, 2.47.[10] Thus, both the trans and cis units exist preferentially as comformers A and D in which the exocyclic oxygen atoms in the backbone chain are located in the axial position of the tetrahydropyran ring (anomeric effect[11]). In these two conformers, each anomeric proton occupies the equatorial position, so that the ^1H NMR coupling constants between the anomeric hydrogen and the adjacent protons should be relatively small (Figure 1).

In order to assign the two anomeric proton signals a and a′, the peak area ratio of the two peaks $A_{a'}/A_a$ was measured and compared for the polymers prepared at different temperatures. The $A_{a'}/A_a$ ratio varied from 22/78 for the polymer obtained at −90 °C to 41/59 for the polymer prepared at −30 °C. As S_N2 type propagation involving the C(1)–O(2) bond cleavage of the growing oxonium ion of **5** leads to polyester exclusively consisting of the trans unit, the coexistence of both the trans and cis units seems to indicate that S_N1 type propagation involving the oxacarbenium ion of **5** concurrently occurs along with the S_N2 type propagation in the cationic polymerization of **5**. Alternatively, in view of the fact that the polymer of **5** is a poly(acetal ester) which readily undergoes acid-catalyzed transacetalization, the formation of the cis units in the polymer can be accounted for also by the S_N2 type propagation followed by transacetalization of the resulting polymer. Although there still remains some uncertainty as to the mechanism of the polymerization, the propagation proceeds primarily through the S_N2 type C(1)–O(2) bond scission[6] to yield polymers containing a larger proportion of the trans unit at lower temperature where transacetalization or S_N1 type propagation is of less significance. Therefore, judging from the temperature dependence of the $A_{a'}/A_a$ values we assigned the stronger peak a appearing at δ 6.08 to the anomeric proton of the trans unit and the weaker peak a′ at δ 6.02 to that of the cis unit. Similarly, the peaks d at δ 3.76 and d′ at δ 3.82 were assigned to the methoxy protons of the pendant ester groups in the trans and cis units, respectively.

The proportion of the cis unit in the polymer tends to increase with the rise in polymerization temperature, but the tendency is not so remarkable as that found in the polymerization of the unsubstituted bicyclic lactone **1**, where the proportion of the cis unit increased from 11% for a polymer obtained at a low conversion at −90 °C to 76% for a polymer at 0 °C.[6] This is interpretable in terms of the free energy difference between the trans and cis units: for polyester **6** having pendant ester groups, the free energy difference should be small because of the very similar structures of the trans and cis units, whereas for polyester **2**, the cis unit having its exocyclic oxygen in the axial position of the tetrahydropyran ring is energetically more stable than the trans unit with the corresponding oxygen in the equatorial position (anomeric effect).

Figure 2 shows the ^{13}C NMR spectrum of polyester **6** prepared at −60 °C with boron trifluoride etherate as the initiator. There are only eight signals assignable to the respective carbons in the polymer as shown in Figure 2. At a first glance, it looks strange because the ^1H NMR

Table II
Copolymerization of 2,6-Dioxabicyclo[2.2.2]octan-3-one (1) with 4-Methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one (5)[a]

1, mmol	5, mmol	mol fract 5 in feed	solv, mL	time, min	yield,[b] %	mol fract 5 in copolymer[c]	$M_n{}^{b,d} \times 10^{-4}$
5.0	0	0	4.5	15	95	0	11
4.5	0.5	0.10	4.5	15	87	0.05	3.7
7.0	3.0	0.30	9	15	69	0.06	2.2
2.0	2.0	0.50	4.5	5	45	0.09	6.3
1.6	2.4	0.60	4.5	7	30	0.12	2.0
1.2	2.8	0.70	4.5	10	39	0.37	4.8
0.6	2.4	0.80	4.5	12	32	0.49	1.6
0.3	2.7	0.90	4.5	15	59	0.84	9.7
0	3.0	1	4.5	60	73	1	5.6

[a] Solvent, dichloromethane; initiator, BF_3OEt_2, 0.05 mmol; temperature, −60 °C. [b] Methanol-insoluble polymer. [c] By ^{1}H NMR spectroscopy. [d] By gel permeation chromatography (polystyrene standard).

spectrum clearly indicates the presence of both the trans and cis units. However, as described above, the prevailing trans and cis units A and D are structurally very similar, and hence the chemical shift differences between the corresponding carbons in these two units are so slight that the trans and cis units are not differentiated in the ^{13}C NMR spectrum taken at 50 MHz.

Copolymerization. Copolymerization of 1 with 5 was undertaken in dichloromethane at −60 °C with boron trifluoride etherate as the initiator. Some of the results of the copolymerization are presented in Table II.

The copolymers thus obtained were white solids having number-average molecular weights ranging from 2.2×10^4 to 9.7×10^4. They gradually decomposed at 143–155 °C (DSC) irrespective of the composition. Their solubility was similar to that of the homopolymer of 5. Even the incorporation of only 5 mol % of the 4-methoxycarbonyl derivative 5 into the copolymer markedly improved the solubility in comparison with that of the homopolymer of 1. This is a strong indication that statistically random copolymers were produced in this copolymerization. Further confirmative evidence was provided by the ^{13}C NMR spectrum of the copolymer, in which there appeared several new signals assignable to the carbons in the crossover diads of 1 and 5, besides the signals appearing in the ^{13}C NMR spectra of the two homopolymers.

It is readily noticeable from the data given in Table II that the unsubstituted bicyclic lactone 1 exhibits a much higher reactivity than its 4-methoxycarbonyl derivative 5. It is to be noted here that the present copolymerization is, strictly speaking, a quaternary system as both 1 and 5 are racemic monomers. Thus, in their copolymerization as well as in homopolymerization, propagation of a given growing chain end with one of the antipodes of monomer occurs at a different rate from propagation of the same growing chain end with the other antipode of the same monomer. In fact, this has been frequently observed in the cationic ring-opening polymerization of racemic bicyclic acetals with conventional Lewis acid initiators, giving rise to polymers rich in isotactic sequences.[12–16]

Therefore, accurate monomer reactivity ratios in the present copolymerization cannot be calculated by conventional copolymerization equations for binary systems. However, as a rough approximation, the apparent monomer reactivity ratios were estimated to be $r_1(1) = 17 \pm 4$ and $r_2(5) = 0.3 \pm 0.1$ by the integral form of the Mayo–Lewis equation, on the assumption that the aforementioned difference in the reactivity toward a growing chain end of a given chirality between the antipodes of a monomer is negligible compared with the large difference in the reactivity between the two monomers. The estimated values clearly show that the methoxycarbony group on the 4-position of 5 markedly reduces the polymerizability of the lactone ring.

Rate constants of acid-catalyzed hydrolysis have been taken as a measure of reactivity in cationic ring-opening polymerization of bicyclic acetals.[17–19] In fact, the relative reactivities for bicyclic acetals with different skeletons span more than 5 powers of 10, and these differences were correlated with ring strain and Eliel's "rabbit-ear" effect.[21] The rate of dichloroacetic acid-catalyzed hydrolysis of 5 was measured in a mixture of deuterioacetone-d_6 and deuterium oxide (4:1 (v/v)) at 25 °C by monitoring the change of the relative intensity of the acetal proton signal of 5. The first-order rate constant was 0.67×10^{-5} s^{-1}, appreciably lower than that for 1 under the identical conditions (5.6×10^{-5} s^{-1}).[7] This difference is in accord with the general tendency that hydrolysis is more difficult as the substitutions on the lactone ring increase.[22] In comparison with base-catalyzed hydrolysis, acid-catalyzed hydrolysis of ester is in general less sensitive to inductive effects of polar substituents on the acyl moiety.[23] This trend originates from two opposing factors. Thus, an electron-withdrawing group decreases the proton acceptability of the carbonyl oxygen of the ester on the one hand, but it increases the electrophilicity of the carbonyl carbon of the ester and hence the tendency to combine with a water molecule on the other hand. In the hydrolysis of 1 and 5, however, a water molecule adds onto the acetal carbon of the protonated lactone, not onto the carbonyl carbon. Therefore, the former factor operates predominantly to decrease the rate of the acid-catalyzed hydrolysis of 5 having an electron-withdrawing methoxycarbonyl group at the 4-position.

Hydrolysis of Polyesters. In order to shed light on the molecular structure–hydrolytic reactivity relationship for the structurally related polyesters 2, 4, and 6, acid-catalyzed hydrolysis of these polyesters in a heterogeneous state was undertaken in 0.001 N hydrochloric acid at 60 °C. Films (thickness, 60–80 μm) were employed for polyesters 2 and 6, whereas powdery samples were used for polyester 4, which was incapable of forming a film on account of its relatively low molecular weight. The degree of hydrolysis was evaluated by the quantitative determination of liberated carboxylic acids in aqueous solutions by UV spectroscopy in combination with the molecular weight determination of residual water-soluble polymers by gel permeation chromatography.

Figure 3 represents the changes in the number-average molecular weight of the polyesters with reaction time in the acid-catalyzed hydrolysis. For polyesters 2 and 6, sudden depression in the molecular weight was observed at the very beginning of the hydrolysis, followed by a gradual molecular weight decrease. This phenomenon implies that the polymer chains do not depolymerize from the terminal units but they are cleaved randomly.

Figure 4 depicts the degree of hydrolysis as a function of reaction time for the three polyesters. 6-Hydroxy-

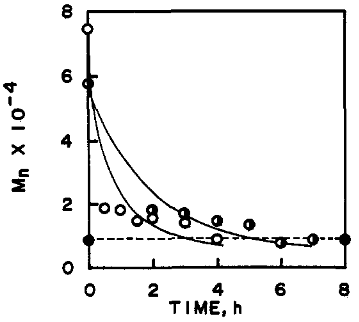


Figure 3. Changes in the molecular weight of polyesters with time in the heterogeneous acid-catalyzed hydrolysis. Polymer, 25 mg, 0.001 N HCl, 5 mL; temperature, 60 °C. (○) Polyester 2 (M_n = 7.0 × 10^4), thickness of film, 80 μm; (◑) polyester 6 (M_n = 5.6 × 10^4), thickness of film, 60 μm; (●) polyester 4 (M_n = 0.9 × 10^4), powder.

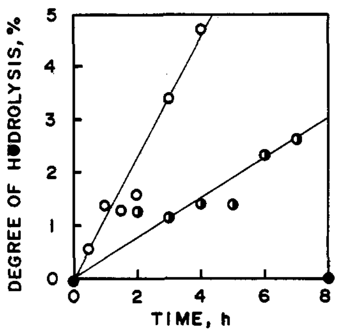


Figure 4. Degree of hydrolysis (percent) as a function of reaction time in the heterogeneous acid-catalyzed hydrolysis of polyesters. Polymer, 25 mg; 0.001 N HCl, 5 mL; temperature, 60 °C. (○) polyester 2 (M_n = 7.0 × 10^4), thickness of film, 80 μm; (◑) polyester 6 (M_n = 5.6 × 10^4), thickness of film, 60 μm; (●) polyester 4 (M_n = 0.9 × 10^4), powder.

tetrahydropyran-3-carboxylic acid and methyl hydrogen 6-hydroxytetrahydropyran-3,3-dicarboxylate 10 were liberated from polyester 2 and polyester 6, respectively. As in the hydrolysis of bicyclic lactones 1 and 5, pendant methoxycarbonyl groups lowered the rate of hydrolysis of polyester 6 compared with that of polyester 2: polyester 6 was hydrolyzed about 3 times as slowly as polyester 2.[24] In contrast to polyesters 2 and 6, neither reduction of the molecular weight nor formation of 5-hydroxytetrahydropyran-2-carboxylic acid was detected for polyester 4 even after reaction for 8 h. As the hydrolysis of polyester 4 was carried out in a powdery state, while the hydrolysis of polyesters 2 and 6 in films, an exact comparison cannot be made, but the observed remarkable difference in the acid-catalyzed hydrolysis principally arises from the absence of acetal–ester linkages in polyester 4, in addition to its partial crystallinity as revealed by X-ray diffraction. More quantitative analysis on the hydrolytic reactivities of these polyesters will be the subject for future investigation.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM FX-200 spectrometer operating at 200 (^{1}H) and 50 MHz (^{13}C), respectively. Deuteriochloroform and tetramethylsilane were used as the solvent and internal reference. IR spectra were measured with a Jasco A-3 spectrophotometer. Molecular weights of the polymers were determined by using a Hitachi 634A gel permeation chromatograph (column, Shodex A80M, 1 m; eluent, chloroform; polystyrene standard).

Preparation of Methyl Hydrogen 6-Methoxytetrahydropyran-3,3-dicarboxylate (10). A solution of potassium hydroxide (6.05 g, 0.091 mol) in methanol (45 mL) was slowly added to a solution of dimethyl 6-methoxytetrahydropyran-3,3-dicarboxylate[6] (9), (21.1 g, 0.0091 mol) in methanol (40 mL) at room temperature. The reaction mixture was allowed to stand overnight at room temperature and then it was subjected to rotary evaporation. The residue was dissolved in 60 mL of water, followed by extraction with two 40-mL portions of diethyl ether to remove unreacted diester. The aqueous layer was slightly acidified with 6 N hydrochloric acid (15.2 mL) and extracted with three 45-mL portions of diethyl ether. The combined ether extracts were washed with saturated aqueous sodium chloride (40 mL) and dried over anhydrous magnesium sulfate. Rotary evaporation of the solvent gave 10 as a viscous oil: yield 17.2 g (87%); IR (CH_2Cl_2) 1738 ν(C=O, ester), 1710 ν(C=O, carboxylic acid), 1120 ν(COC) cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 7.3–7.8 (br, 1 H, COOH), 4.55–4.63 (m, 1 H, H-6), 4.03–4.23 (m, 2 H, H-2), 3.56, 3.60 (s, 3 H, $COOCH_3$), 3.32, 3.40 (s, 3 H, OCH_3), 1.6–2.3 (m, 4 H, 2H-4, 2H-5); ^{13}C NMR ($CDCl_3$) δ 174.50, 174.31 (COOH), 169.68 (*C*$OOCH_3$), 98.53, 98.29 (C-6), 62.52, 62.28 (C-2), 55.21, 55.11 (COO*C*H_3), 53.36, 52.97 (OCH_3), 52.71 (C-3), 26.51 (C-5), 24.56, 24.32 (C-4). The appearance of a pair of signals with slightly different chemical shifts is ascribable to the coexistence of the stereoisomers.

Preparation of 4-Methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one (5). A solution of 10 (17.2 g, 0.079 mol) and *p*-toluenesulfonic acid monohydrate (0.150 g, 0.80 mmol) in dry toluene (800 mL) was allowed to reflux through a Soxhlet extractor containing a thimble charged with molecular sieves type 4A. After the solution was cooled to room temperature, anhydrous potassium carbonate (5 g) was added to the solution, and the mixture was stirred at room temperature for 30 min. The mixture was filtered and the filtrate was subjected to rotary evaporation to afford a slightly yellow wax. Recrystallization from diethyl ether gave white crystals: yield 83%; mp 91–92 °C (DSC); IR (KBr) 1748 ν(C=O, lactone), 1728 ν(C=O, ester), 1270 ν(COC, ester), 1178 ν(COC, lactone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.72 (t, *J* = 1.7 Hz, 1 H, H-1), 4.40 (dd, *J* = 3.3 Hz, *J* = 9.0 Hz, 1 H, H-5_{eq}), 4.06 (d, *J* = 9.0 Hz, 1 H, H-5_{ax}), 3.83 (s, 3 H, OCH_3), 2.11–2.42 (m, 4 H, 2 H-7 and 2 H-8; ^{13}C NMR ($CDCl_3$) δ 168.63 (C=O, lactone), 166.96 (*C*$OOCH_3$), 97.69 (C-1), 67.44 (C-5), 52.88 (OCH_3), 48.89 (C-4), 26.03 (C-7), 23.43 (C-8); MS *m/e* 186, 158, 142, 114. Anal. Calcd for $C_8H_{10}O_5$: C, 51.61; H, 5.41. Found: C, 51.54; H, 5.42.

Polymerization of 4-Methoxycarbonyl-2,6-dioxabicyclo[2.2.2]octan-3-one (5). Cationic homopolymerization of 5 was carried out in dichloromethane at temperatures between −90 and −30 °C with boron trifluoride etherate and phosphorus pentafluoride as initiators. A high-vacuum technique was employed for the polymerization. After the polymerization was terminated by the addition of a small amount of pyridine, the reaction mixture was poured into a large volume of methanol to precipitate a polymer. It was purified by repeated reprecipitation from dichloromethane and methanol as a solvent–precipitant pair and dried under reduced pressure to a constant weight: mp (decomp.) 142–152 °C (DSC); IR (film) 1740 ν(C=O), 1260 ν(COC, ester) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.09 (H-2, trans unit), 6.02 (H-2, cis unit), 3.9–4.4 (H-6), 3.82 (OCH_3, cis unit), 3.76 (OCH_3, trans unit), 2.37 (H-3_{eq}), 2.09 (H-3_{ax} and H-4_{eq}), 1.77 (H-4_{ax}); ^{13}C NMR ($CDCl_3$) δ 168.95 (C=O, main chain), 167.05 (*C*$OOCH_3$), 92.29 (C-2), 63.78 (C-6), 53.07 (C-5), 52.88 (OCH_3), 25.13 (C-3), 23.79 (C-4). (The numbering is based on the IUPAC nomenclature for macromolecules.) Anal. Calcd. for $(C_8H_{10}O_5)_n$: C, 51.61; H, 5.41. Found: C, 51.87; H, 5.42.

Copolymerization of 1 with 5 was carried out in a similar manner at −60 °C with boron trifluoride etherate as the initiator. Copolymer composition was determined by ^{1}H NMR spectroscopy from the relative peak areas of the anomeric protons of both monomeric units and the methine proton adjacent to the carbonyl group of the monomeric unit of 1.

Acid-Catalyzed Solvolysis of Bicyclic Lactone 5. The rate of the acid-catalyzed solvolysis of 5 was determined at 25 °C in a mixture of acetone-d_6 and deuterium oxide (4:1 (v/v)) in the presence of dichloroacetic acid as catalyst. The initial concentrations of 5 and dichloroacetic acid were 1.0 and 0.05 mol/L, respectively. The reaction was followed by monitoring the change of the acetal proton signal in ^{1}H NMR spectra.

Acid-Catalyzed Hydrolysis of Polyesters. A sample of polyester (25 mg; films of thickness of 60–80 μm for polyesters 2 and 6, and powder for polyester 4) was placed in each of several test tubes, to which 0.001 N hydrochloric acid (5 mL) was added. The test tubes were allowed to stand in a water bath thermostated at 60 °C. At specified intervals, one of the test tubes was taken out and cooled. The aqueous solution was separated from the insoluble material by decantation. The carboxylic acid content of the aqueous solution $[\mathrm{COOH}]_{\mathrm{aq}}$ was measured by UV spectroscopy using the absorption at 210 nm ($\epsilon = 71$). The water-insoluble material was washed with water, dried under vacuum, and weighed. The number-average molecular weight was determined by gel permeation chromatography. The carboxylic group content of the water-insoluble material $[\mathrm{COOH}]_{\mathrm{insol}}$ was estimated from its weight and molecular weight assuming that an ester bond cleavage in the main chain produced one carboxylic group. The degree of hydrolysis (in percent) was represented as the percentage of the total moles of the liberated carboxylic groups ($[\mathrm{COOH}]_{\mathrm{aq}} + [\mathrm{COOH}]_{\mathrm{insol}}$) to the moles of the monomeric unit in feed.

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Registry No. **1**, 100190-12-3; **1** (homopolymer), 100190-22-5; (**1**) (**5**) (copolymer), 107711-19-3; **3**, 100762-90-1; **5**, 107711-15-9; **5** (homopolymer), 107711-18-2; **6**, 107711-21-7; **9**, 100190-14-5; **10**, 107711-16-0; *p*-TSA, 104-15-4; PF_5, 7647-19-0; $\mathrm{BF}_3\mathrm{OEt}_2$, 109-63-7.

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(24) Under the conditions employed, the pendant methoxycarbonyl groups in polyester **6** might be hydrolyzed, but the extent was too small to be detected spectroscopically.

"Defect-Free", Crystalline Aromatic Poly(ether ketones): A Synthetic Strategy Based on Acetal Monomers

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ABSTRACT: A novel synthesis of high molecular weight, crystalline aromatic poly(ether ketone) 1 [poly(oxybenzophenone), mp 370 °C] has been developed which minimizes the introduction of chemical defects into the polymer backbone. Consequently, poly(ether ketone) **1K** exhibited higher crystallinity, as evidenced by modulus and thermal characteristics, than poly(ether ketones) prepared by direct methods. Solution and solid-state $^{13}\mathrm{C}$ NMR spectra are consistent with a highly uniform para-oriented backbone and with the observed crystallinity. The synthetic strategy involved the preparation of an amorphous precursor poly(ketal ketone) (**3b**) under mild reaction conditions by nucleophilic displacement polycondensation of acetal monomer **2b** [2,2-bis(4-hydroxyphenyl)-1,3-dioxolane] with 4,4′-difluorobenzophenone at 150–220 °C in a dipolar aprotic solvent. Amorphous polymer **3b** was then quantitatively converted to high molecular weight, crystalline, insoluble poly(ether ketone) **1K** by acid-catalyzed hydrolysis under heterogeneous conditions. Reaction temperatures above the polymer T_g were required, which is consistent with a diffusion-limited reaction. Homogeneous hydrolysis in concentrated sulfuric acid (25 °C) was also effective. An improved synthesis of the novel cyclic acetals of 4,4′-dihydroxybenzophenone is also reported which employs a combination of glycol, trialkyl orthoformate, and montmorillonite clay catalyst. The acyclic dimethyl acetal monomer **2a** was found to be unsuitable for the polycondensation because it undergoes an unusual degradation under basic reaction conditions to a postulated quinone methide.

Introduction

The crystallinity of aromatic poly(ether ketones) imparts valuable characteristics, including excellent resistance to solvents, high melting points, and useful properties at temperatures exceeding 250 °C. However, because of their crystallinity and the resultant insolubility, these polymers are also difficult to prepare with sufficiently high molecular weights unless extreme conditions are used.

Friedel–Crafts polycondensations of carboxylic acids or acid chlorides in organic solvents or in polyphosphoric acid

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