Ir analysis showed CH at 3.45 (s) and 3.51 (m), C=O at 5.71 (s) and 5.91 (s).

11-Hydroxymethylethanoanthracene-11-carboxylic Acid (52). A solution of 25.0 g (0.0811 mol) of hydroxy ester **34** and 7.1 g of potassium hydroxide in 50 ml of water and 100 ml of dimethyl sulfoxide[28,29] was heated under nitrogen on the steam bath for 60 hr. A white solid crust formed. The mixture was cooled and filtered. The solid was dissolved in 500 ml of water, extracted three times with 250-ml portions of ether, and acidified with 30 ml of 12 *N* hydrochloric acid. The oil was taken up in two 250-ml portions of ether, dried with magnesium sulfate, and evaporated gently on the steam bath. It was then heated vigorously on the steam bath to drive out the last traces of solvent. Foaming and crystallization occurred. The solid was cooled and broken up to give 16.2 of white solid, mp 90–95°. This was recrystallized from ethyl acetate–hexane (1:1) to give 12.72 g (55.9%) of white crystals, which adhered tenaciously to solvent. Drying for 17 hr in a pistol at 107° (0.5 mm) over P_2O_5 caused a little wax to sublime out. The white crystalline residue of hydroxy acid melted at 146.3–148.0°.

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found (using WO_3): C, 77.01, 76.93; H, 5.71, 5.70.

Ir analysis showed OH at 2.95 (m), CH at 3.35 (w), 3.45 (s), and 3.51 (w), HOOC at 3.7–4 (jagged, w), C=O at 5.82 (s); nmr (THF-*d*) ArH at 2.85 (m), bridgehead H-9 at 5.38 (s), H-10 at 5.75 (apparent t, separation 2 cps), OCH_2 at 6.69 and 6.90 (J = 11 cps, 2 H), bridgehead H-11 at 7.50 and 8.5 (J_{gem} = 14 cps, J_{vic} = 3 cps, 2 H), possible OH at 8.01 (s).

Triphenylphosphoniopivalate, $(C_6H_5)_3P^+CH_2C(CH_3)_2COO^-$. To 104.9 g of triphenylphosphine at 160° was added with stirring under nitrogen a solution of 18.1 g of bromopivalic acid in 10.0 g of pivalolactone during 31 min. The solution was held at 160° for 8 hr. The cooled reaction mixture was ground up, extracted thoroughly with ether, and filtered. The insoluble solid weighed 12.2 g.

Of this solid, 6.1 g was heated for 2 hr with 60 ml of 48% hydrobromic acid to hydrolyze any oligomers. The cooled mixture was washed twice with 50-ml portions of chloroform to remove triphenylphosphine and its hydrobromide. The aqueous extract was neutralized with sodium bicarbonate and extracted twice with 100-ml portions of methylene chloride. Drying and evaporation left 1.41 g of betaine, mp 207–217° (bubbles). The ir spectrum showed carboxylate absorption at 6.25 μ.[30,31] Recrystallization from ethyl acetate gave 0.37 g (1.4% yield) of pure betaine, mp 217–220° (bubbles). It was dried at 80° (0.3 mm) over P_2O_5.

Anal. Calcd for $C_{23}H_{23}O_2P$: C, 76.22; H, 6.40; P, 8.55. Found: C, 76.68, 76.45; H, 6.39; P, 7.41, 7.98, 8.73, 8.26.

TGA measurements of solid samples showed that weight loss from this betaine began at 200°, whereas tetrabutylammonium pivalate began at 137°.

The betaine was an active catalyst for pivalolactone polymerization. For polymerizations of the slow spirolactones it was used as a 0.0094 *M* solution in γ-butyrolactone.

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(28) E. Tommila and M. L. Murto, *Acta Chem. Scand.*, **17**, 1947 (1963).
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The Nucleophile-Initiated Polymerization of α,α-Disubstituted β-Lactones

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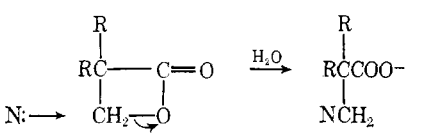
ABSTRACT: The rate constants for reactions of α,α-dialkyl-β-lactones with quaternary ammonium carboxylates in organic solvents were measured. The heat of polymerization of pivalolactone was −20.1 kcal mol^{-1}, allowing calorimetric determination of the rate constants. The rates were much higher in acetonitrile or tetrahydrofuran than in water and correspond to the fastest ring opening polymerizations recorded. Polar substituents in the alkyl groups accelerated the rates, whereas branched alkyls or bridged rings retarded. Pivalate ion was the most reactive nucleophile, followed by acetate, fluoride, and benzoate. Other halide ions and *p*-toluenesulfonate were extremely slow. Chloropivalolactone reacted with carboxylates to generate chloride ion and an intermediate acyloxypivalolactone, a reaction which can lead to branching.

Physical organic investigations[2] have shown that a β-lactone in aqueous solution can react at any of three places in the molecule. Strong acid protonates the carbonyl oxygen while alkali attacks the C=O at carbon. In intermediate pH ranges, other anions or water itself attack the CH_2 group with alkyl–oxygen cleavage (SN2), in general with simple second-order



(1) Department of Chemistry, University of Arizona, Tucson, Ariz. 8572.
(2) For a good summary of β-lactone chemistry, see Y. Etienne and N. Fischer in "Heterocyclic Compounds with 3- and 4-Membered Rings," A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1964, pp 729–884.

kinetics. The reactivity of various halide and carboxylate nucleophiles[3a] follows the familiar Swain–Scott relationship[3b] $I^- > Br^- > Cl^- > CH_3COO^- > F^-$, with n values 5.04, 3.89, 3.04, 2.72, and 2.0,[4] respectively. However, little is known of β-lactone reactivity in organic solvents. The present investigation was aimed at elucidating one such reaction, namely nucleophile-initiated polymerization of the following series of β-lactones: α-methyl-α-alkyl-β-lactones containing increasingly branched alkyl groups; α,α-dialkyl-β-lactones in which the two alkyls were the same; β-lactones containing $ClCH_2$, FCH_2, C_6H_5, and $C_6H_5CH_2$ as polar substituents; and mono- and bicyclic spirolactones.

Acetonitrile was chosen as solvent for most of the work because its high dielectric constant (D.C. 34.6 at 25°) makes it a good solvent for salts and minimizes ion-pairing effects. Moreover, a large amount of information on conductance and basicities in acetonitrile is available. A few runs were also carried out in tetrahydrofuran (D.C. 7.4 at 25°).

Tetraalkylammonium salts were used as initiators in these kinetic studies. The halides, except for fluorides, were readily available. Quaternary ammonium carboxylates[5,6] and fluorides[6,7] have been used to advantage on occasion in synthesis work but have often been obtained as hydrates. We were able to recrystallize them from mixed organic solvents and obtain them in crystalline, anhydrous form.[8] We were less successful with fluorides.

Results and Discussion

Heat of Polymerization. The β-lactones evolved a considerable amount of heat during polymerization. Quantitative determination of this heat of polymerization for pivalolactone was carried out by determining heats of combustion for liquid pivalolactone and for solid polypivalolactone and finding the difference between them (Table I). The heat of polymerization ΔH_{1c} was −20.1 kcal mol^{-1}. This value is about equal to that found for propiolactone, −19.2 kcal mol^{-1},[9] whereas between oxetane (−19.2 kcal mol^{-1}) and 3,3-dimethyloxetane (−15.9 kcal mol^{-1}),[10] a numerical decrease is noted.

A cycle similar to that given for polymerization of propiolactone[9a] was constructed for pivalolactone as follows. The strain energy was estimated using the $\Delta H^\circ_{f,g}$ value of −8.6 kcal mol^{-1} for 1,1-dimethylcyclobutane given by Dainton and Ivin[11] and the $\Delta\Delta H^\circ_{f,g}$ value of −71.0 kcal mol^{-1} given by Sunner, *et al.*,[9b] to give a calculated $\Delta H^\circ_{f,g}$ = −79.6 kcal mol^{-1} as against an experimental value of −84.1 kcal mol^{-1}. The strain energy of pivalolactone, 20.5 kcal mol^{-1}, is slightly lower than that of propiolactone, 22.5 kcal mol^{-1}. The cycle then becomes (all values in kilocalories per mole)

$$\begin{array}{ccc} \text{PVL (g)} & \xrightarrow{-20.5} & \text{poly-PVL (g)} \\ \uparrow +10.1 & & \downarrow (-9.7) \\ \text{PVL (l)} & \xrightarrow{-20.1} & \text{poly-PVL (c)} \end{array}$$

giving a reasonable value of −9.7 kcal mol^{-1} for condensation of gaseous polymer.

TABLE I
THERMOCHEMICAL QUANTITIES FOR POLYMERIZATION OF PIVALOLACTONE

Pivalolactone

ΔE_c = −6482.3 cal g^{-1}
= −6482.3
= −6474.5
= −6479.2
ΔE_c = −6479.6 cal g^{-1} (av)
ΔE_c = −648.72 kcal mol^{-1}
$\Delta H_{c,l}$ = −649.31 kcal mol^{-1}
$\Delta H^\circ_{f,l}$ = −94.43 kcal mol^{-1}
ΔH_v = 10.14 kcal mol^{-1}
$\Delta H^\circ_{f,g}$ = −83.55 kcal mol^{-1}

Polypivalolactone

ΔE_c = −6277.8 cal g^{-1}
= −6276.6
= −6286.7
ΔE_c = −6280.4 cal g^{-1} (av)
ΔE_c = −628.73 kcal mol^{-1}
$\Delta H^\circ_{c,c}$ = −628.97 kcal mol^{-1}
$\Delta H^\circ_{f,c}$ = −114.56 kcal mol^{-1}

Pivalolactone (l) → polypivalolactone (c)

$\Delta H^\circ_{l,c}$ = −20.1 kcal mol^{-1}

Polymerization Kinetics. The above large heat of polymerization enabled a calorimetric method[12,13] to be used to determine the polymerization rates. For calculations, the simplest polymerization kinetics scheme describes the results. Here the initiator I

$$I + M \xrightarrow{k_I} IM_1 \text{ (initiation)}$$

$$IM_1 + M \xrightarrow{k_P} IM_2, \text{ etc. (propagation)}$$

attacks the β-lactone M to give the β-substituted carboxylate, which attacks further monomer molecules to cause chain growth. No termination or chain transfer is involved for these lactones.[14–16]

When pivalate ion is used as the initiator in acetonitrile solution and no polar substituents are present, k_P will be slightly less than k_I. Models make it evident that this ion is sterically identical with the propagating carboxylate ion, and a mild (not >20%) rate-retarding

(3) (a) P. D. Barlett and G. Small, *J. Amer. Chem. Soc.*, **72**, 4867 (1950); (b) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).
(4) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 161.
(5) N. A. Hughes and P. R. H. Speakman, *J. Chem. Soc.*, 2236 (1965).
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(7) W. T. Miller, Jr., H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, **82**, 3091 (1960).
(8) However, N. L. Cox, C. A. Kraus, and R. M. Fuoss [*Trans. Faraday Soc.*, **31**, 749 (1935)] prepared and recrystallized tetrabutylammonium acetate from benzene–petroleum ether (bp 30–60°).
(9) (a) B. Boyesso, Y. Nakase, and S. Sunner, *Acta Chem. Scand.*, **20**, 803 (1966); (b) M. Mansson, Y. Nakase, and S. Sunner, *ibid.*, **22**, 171 (1968).
(10) J. B. Rose, *J. Chem. Soc.*, 546 (1956).
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(15) Y. Yamashita, Y. Ishikawa, T. Tsuda, and S. Miura, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **66**, 104 (1963).
(16) Y. Yamashita, Y. Ishikawa, and T. Tsuda, *ibid.*, **67**, 252 (1964).

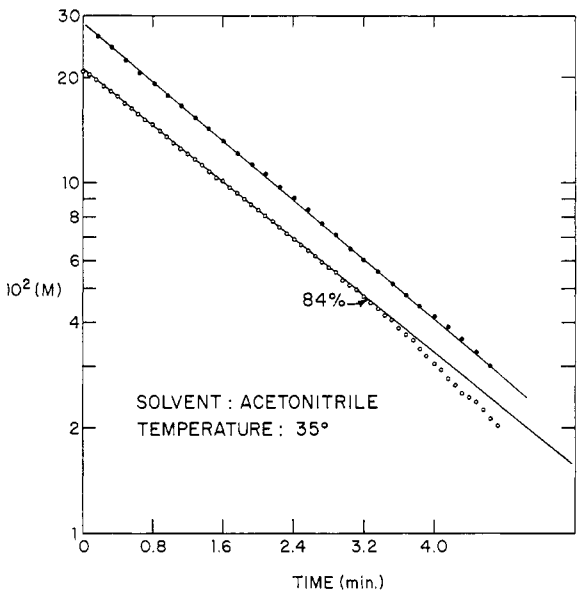
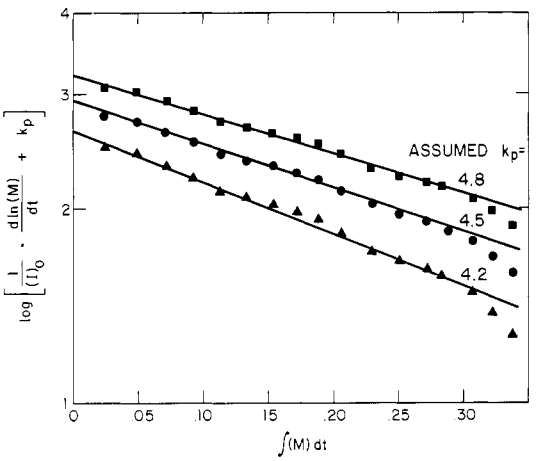


Figure 1. Reactions of α-methyl-α-*n*-propylpropiolactone with tetraethylammonium pivalate.



ASSUMED k_p	INTERCEPT	INTERCEPT k_I	SLOPE	SLOPE k_I
▲ 4.2	2.63	1.57	-.82	1.90
● 4.5	2.92	1.58	-.68	1.58
■ 4.8	3.20	1.60	-.61	1.41

Figure 2. Example of treatment of data to obtain k_I and k_P; α-methyl-α-*n*-propylpropiolactone initially 0.0785 *M*; tetramethylammonium benzoate initially 0.0631 *M*; acetonitrile, 35.0°. Correct value of k_p = 4.5.

effect of the acyloxy group in the latter is expected. Under these circumstances the β-lactone will polymerize according to approximate first-order kinetics. A good evaluation of k_I only was gotten from such plots (Figure 1).

For other initiators for which k_I differed markedly from k_P, the treatment of Beste and Hall[17] was used to obtain both values. An example of this calculation is given in Figure 2.

Effects of Structure on Reactivity of β-Lactones. The rate constants obtained using tetraethylammonium pivalate as initiator and acetonitrile as solvent are given in Table II. For reasons described above, only k_I values are given for this initiator.

The rate constant for the parent propiolactone is somewhat uncertain. The results did not fit the kinetics scheme, perhaps because of chain transfer[14-16] and a rate constant is included only for comparison. (Second-order plots, implying small k_P, were nearly linear, and the initial values were taken as k_I.) The initiation rate constant is not depressed by the introduction of two α-methyl groups. The numerical value for pivalolactone, 0.36 M^{-1} sec^{-1}, found in the present work for acetonitrile at 35°, greatly exceeds that found by Fischer,[18] 0.028 M^{-1} sec, for ethyl acetate solution at 90°. Even with allowance for possible solvent effect, the present value is preferred because it was obtained in a stirred, homogeneous medium. Substitution by larger alkyl groups results in a marked lowering of the rate constant. Examination of models shows that alkyl–alkyl crowding between pivalate and β-lactone can be avoided in each case, so the steric hindrance must be provided by the alkyl groups against the incoming carboxylate ion. Similarly, while the cyclopentane spirolactone is reactive, the more bulky spiro rings drastically lower reactivity (the drop being a rate effect, and not an unfavorable equilibrium, because all the lactones do polymerize). On the other hand, polar substituents such as phenyl and chloromethyl increase the rate constants. Yamashita and coworkers[19] showed recently that α,α-bischloromethylpropiolactone is at least five times as reactive as propiolactone in carboxylate-propagated polymerization, and this agrees with our results. These over-all trends are in accord with theoretical calculations of Fukui and coworkers,[20] who calculated the electron density at the β-carbon for several α,α-disubstituted β-lactones, and with the effects of alkyl groups on SN2 reactions, if the two methyl groups in pivalolactone are regarded as "pinned back."[21]

Experiments using tetrahydrofuran as solvent (Table II) utilized lower pivalate concentration because the rates were higher in this solvent. Under these conditions, fast initiation was followed by a long linear portion of the ln (M) *vs. t* plot corresponding to the propagation reaction.

Effect of Additives. Addition of inert salts raised the rate constants slightly while small concentrations of water lowered them (Table III). *p*-Toluenesulfonate ion itself is an extremely feeble initiator; perchlorate ion is inert.

Effect of Other Carboxylates. When k_I and k_P were calculated for pivalolactone, the results (given in Table IV) showed pivalate > acetate > benzoate, which is understandable in terms of the electron-attracting properties of the substituents. Evidently steric interactions with the methyl groups of the pivalate ion are not serious. As it should be, k_P appeared to be about the same for each initiator. Similarly, the propagation rate constant obtained from the use of benzoate ion agreed with that from pivalate ion for α-methyl-α-*n*-propylproprolactone in tetrahydrofuran.

(17) L. F. Beste and H. K. Hall, Jr., *J. Phys. Chem.*, **68**, 269 (1964).
(18) N. Fischer, Thesis, Paris, 1959.
(19) Y. Yamashita, T. Tsuda, H. Ishida, A. Uchikawa, and Y. Kuriyama, *Makromol. Chem.*, **113**, 139 (1968).
(20) K. Fukui, H. Kato, T. Yonezawa, and S. Okamura, *Bull. Chem. Soc. Jap.*, **37**, 904 (1964).
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TABLE II
RATE CONSTANTS FOR REACTION OF α,α-DISUBSTITUTED β-LACTONES WITH TETRAALKYLAMMONIUM[a] PIVALATES

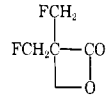
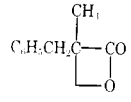
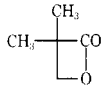
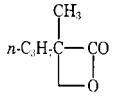
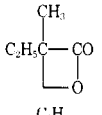
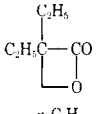
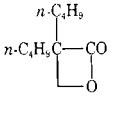
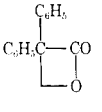
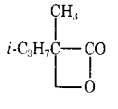
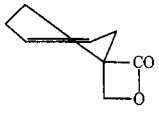
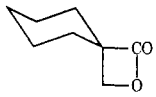
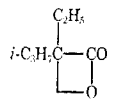
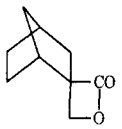
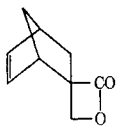
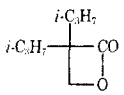
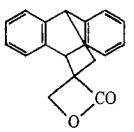
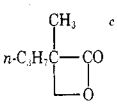
Lactone	Temp, °C	Initial concn of lactone (solvent acetonitrile)	Initial concn of initiator (solvent acetonitrile)	k_1, M^{-1} sec^{-1} (from initial slope)	Av	k_p, M^{-1} sec^{-1} (from final slope)	Av
	35.0	0.01	0.03	>1.0			
	35.0	0.0249	0.0468	0.82			
	35.0	0.0122	0.0468	0.78	0.84 ± 0.06		
	35.0	0.0136	0.0955	0.93			
	25.0	0.0263	0.0885	0.15[b]	0.16 ± 0.01		
	25.0	0.0317	0.0456	0.16[b]			
	28.0	0.0384	0.0456	0.20[b]	0.20		
	35.0	0.0689	0.0468	0.30[b]	0.30		
	25.0	0.0377	0.0885	0.10			
	25.0	0.0434	0.0456	0.14	0.13 ± 0.02		
	25.0	0.0345	0.0456	0.15			
	35.0	0.0276	0.0432	0.30			
	35.0	0.0322	0.0432	0.36	0.36 ± 0.03		
	35.0	0.0381	0.0218	0.41			
	35.0	0.0308	0.0468	0.37			
	35.0	0.0635	0.0468	0.35	0.38 ± 0.02		
	35.0	0.0442	0.0468	0.41			
	35.0	0.0222	0.0467	0.17			
	35.0	0.0249	0.0467	0.16			
	35.0	0.0225	0.0467	0.16			
	35.0	0.0305	0.0955	0.26	0.18 ± 0.02		
	35.0	0.0209	0.0432	0.18			
	35.0	0.0285	0.0432	0.18			
	35.0	0.0328	0.0432	0.16			
	35.0	0.0452	0.0218	0.14			
	50.0	0.0685	0.0423	0.58	0.62 ± 0.04		
	50.0	0.0387	0.0423	0.65			
	35.0	0.0288	0.0927	0.18			
	35.0	0.0433	0.0927	0.19	0.19 ± 0.005		
	35.0	0.0375	0.0221	0.16	0.16		
	35.0	0.0576	0.0221	0.16			
	35.0	0.0521	0.0955	0.18			
	35.0	0.0294	0.0955	0.16	0.16 ± 0.01		
	35.0	0.0623	0.0468	0.13			
	35.0	0.0394	0.0468	0.16			
	35.0	0.0142	0.0927	0.076	0.084 ± 0.08		
	35.0	0.0276	0.0927	0.092			
	50.0	0.0458	0.167	0.15			
	50.0	0.0348	0.167	0.18	0.21 ± 0.04		
	50.0	0.0445	0.0849	0.25			
	50.0	0.0398	0.0849	0.24			
	35.0	0.0380	0.0960	0.029			
	35.0	0.0641	0.0960	0.022	0.026 ± 0.004		
	50.0	0.0130	0.0849	0.068			
	50.0	0.0867	0.0849	0.072			
	50.0	0.0797	0.0167	0.051			
	50.0	0.132	0.0423	0.100	0.073 ± 0.016		
	35.0	0.030	0.0927	0.052	0.049 ± 0.04		
	35.0	0.0450	0.0927	0.045			
	50.0	0.0605	0.0849	0.13			
	50.0	0.0836	0.0849	0.11	0.10 ± 0.020		
	50.0	0.0708	0.167	0.073			
	50.0	0.0516	0.167	0.087			

TABLE II (*Continued*)

Lactone	Temp, °C	Initial concn of factor (solvent acetonitrile)	Initial concn of initiator (solvent acetonitrile)	k_1, M^{-1} sec^{-1} (from initial slope)	Av	k_P, M^{-1} sec^{-1} (from final slope)	Av
	50.0	0.132	0.167	0.038			
	50.0	0.141	0.0849	0.058	0.048 ± 0.008		
	50.0	0.181	0.0849	0.054			
	50.0	0.091	0.167	0.040			
	35.0	0.1	0.1	0.017			
	35.0	0.1	0.1	0.01>			
	35.0	0.1	0.1	0.01≫			
	35.0	0.1	0.1	0.01≫			
	35.0	0.02	0.1	0.01≫			
CH_3I	35.0	0.00911	0.0877	0.68[b]			
	35.0	0.00911	0.0571	0.99[b]	0.89 ± 0.14		
	35.0	0.0113	0.0571	1.0[b]			
 [c]	35.0	0.03154	0.0111			0..	
	35.0	0.03277	0.0111			1.1	
	35.0	0.04705	0.00990			0.80	0.90 ± 0.10
	35.0	0.0203	0.00990			0.95	
	35.0	0.0359	0.00492			0.92	
CH_3I[c]	35.0	0.01	0.00492	>1.5[b]			
CH_3I[d]	35.0	0.0284	0.0105	1.5[b]			
	35.0	0.0550	0.0105	1.3[b]			

[a] Tetraethylammonium pivalate in acetonitrile, tetrabutylammonium pivalate in tetrahydrofuran or benzene. [b] From second-order plot. [c] Solvent tetrahydrofuran. [d] Solvent benzene.

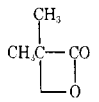
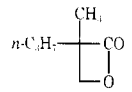
TABLE III

EFFECT OF ADDITIVES ON RATE CONSTANTS FOR α-METHYL-α-*n*-PROPYLPROPIOLACTONE AT 35.0°

Initial lactone concn	Initiator	Initial initiator concn	Additive	Additive concn, M	k_1, M^{-1} sec^{-1}	k_P, M^{-1} sec^{-1}
Varied[a]	$(C_2H_5)_4N^+(CH_3)_3CCOO^-$	Varied	None		0.18[a]	
0.0303[b]	$(C_2H_5)_4N^+(CH_3)_3CCOO^-$	0.0476	$(C_2H_5)_4N^+ClO_4^-$	0.0642	0.24	
0.0771[b]	$(C_2H_5)_4N^+(CH_3)_3CCOO^-$	0.0476	$(C_2H_5)_4N^+ClO_4^-$	0.0642	0.28	
0.0233[b]	$(C_2H_5)_4N^+(CH_3)_3CCOO^-$	0.0438	H_2O	0.050	0.13	
0.0263[b]	$(C_2H_5)_4N^+(CH_3)_3CCOO^-$	0.0438	H_2O	0.050	0.12	
Varied[a]	$(n\text{-}C_4H_9)_4N^+(CH_3)_3CCOO^-$	Varied	None			0.90[a]
0.0312[c]	$(n\text{-}C_4H_9)_4N^+(CH_3)_3CCOO^-$	0.0110	$(n\text{-}C_4H_9)_4N^+$ $p\text{-}C_7H_7SO_3^-$	0.010		0.92
0.0285[c]	$(n\text{-}C_4H_9)_4N^+(CH_3)_3CCOO^-$	0.0110	$(n\text{-}C_4H_9)_4N^+$ $p\text{-}C_7H_7SO_3^-$	0.010		1.29
0.0458[c]	$(n\text{-}C_4H_9)_4N^+(CH_3)_3CCOO^-$	0.0134	H_2O	0.010		0.57
0.0487[c]	$(n\text{-}C_4H_9)_4N^+(CH_3)_3CCOO^-$	0.0134	H_2O	0.010		0.55

[a] From Table II. [b] Solvent acetonitrile. [c] Solvent tetrahydrofuran.

Table IV
Reactivity of Several Carboxylates and Fluoride Ion at 35.0°

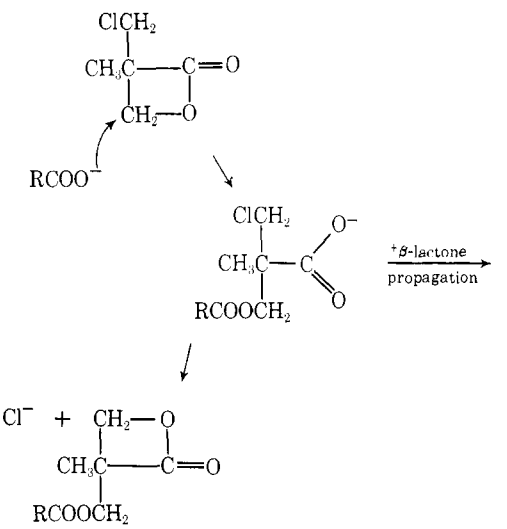
Lactone	Initial concn (solvent acetonitrile)	Initiator	Initial concn (solvent acetonitrile)	From Beste-Hall plot or a linear ln (M) *vs.* t plot k_I, M^{-1} sec^{-1}	k_P, M^{-1} sec^{-1}
	Varied	Tetraethylammonium pivalate	Varied	0.36[a]	
	0.0302	Tetramethylammonium acetate	0.0213	0.22	0.22
	0.0554	Tetramethylammonium acetate	0.0213	0.21	0.21
	0.0498	Tetramethylammonium benzoate	0.0631	0.047	0.12
	0.0864	Tetramethylammonium benzoate	0.0631	0.048	0.11
	0.0477	Tetramethylammonium benzoate	0.0210	0.048	0.13
	0.0602	Tetraethylammonium fluoride	0.0313	0.050[b]	0.12
	0.0602	Tetraethylammonium fluoride	0.0313	0.049[b]	0.12
	Varied	Tetraethylammonium pivalate	Varied	0.18[a]	
	0.0521	Tetramethylammonium acetate	0.0213	0.096	0.13
	0.0549	Tetramethylammonium acetate	0.0213	0.10	0.11
	0.0638	Tetramethylammonium benzoate	0.0631	0.029	0.073
	0.0785	Tetramethylammonium benzoate	0.0631	0.026	0.075
	Varied[c]	Tetrabutylammonium pivalate	Varied		0.90
	0.0344[c]	Tetrabutylammonium benzoate	0.0302	0.33	0.94
	0.0314[c]	Tetrabutylammonium benzoate	0.0300	0.30	0.99

[a] From Table II. [b] Assumes $\Delta H_I = \Delta H_P$, probably satisfactory. [c] Solvent tetrahydrofuran.

Betaines, *i.e.*, inner quaternary ammonium carboxylates, have been cited as initiators for propiolactone polymerization,[22] but require days to reach high molecular weight. This may be due to polar or solubility factors, or to difficulty in maintaining the positive center near the growing carboxylate chain. This low reactivity may be responsible for the low value found by Fischer for the propagation rate constant.

β-Halocarboxylate Anions. Fluoride was as reactive as benzoate ion (Table IV), but chloride, bromide, and iodide ions reacted much too slowly to measure, even at 70°. The observed slowness of chloride relative to carboxylate ions was also shown as follows. Experiments in which the initial concentrations of pivalolactone and tetraethylammonium chloride in acetonitrile varied from 0.1 to 0.01 M showed negligible uptake of chloride ion except at the highest initial concentrations of both reagents. Under those conditions the final concentration of ionic chloride was 0.093 M. Propagation by carboxylate competes successfully with initiation by chloride, so little of the latter is consumed and halide ions are useful initiators.[23] This contrasts with the behavior observed in water solution. However, one cannot conclude that the nucleophilic reactivity of the ions in acetonitrile follows an inverted sequence from that in water, for reasons immediately following.

When treated with tetraethylammonium pivalate in acetonitrile solution, chloropivalolactone reacts more rapidly than pivalolactone, and forms ionic chloride. The explanation is that cyclization of the intermediate β-chloro-β′-pivaloxy anion can occur. Table V presents titrimetric data for this reaction in dilute solution. The final chloride ion concentration approximately equals the initial concentration of whichever reagent was present in deficit, so the cyclization occurs quantitatively in dilute solution. When concentrations are higher, the yield of chloride is not quantitative; polymerization can compete with cyclization. (This cyclization is actually the reaction often used to make β-



(22) Y. Etienne and R. Soulas, *J. Polym. Sci., Part C*, 2, 1061 (1963).
(23) Shell, British Patent 1,028,928 (1966), and French Patent 1,419,642 (1966).

TABLE V
FORMATION OF CHLORIDE ION IN REACTION OF PIVALATE ION WITH CHLOROPIVALOLACTONE[a]

Conditions	(ClPVL)	(Piv^-)	(Cl^-)
$(Piv^-)_0 >$	0.045 → 0	0.094 → 0.021	0 → 0.041
$(ClPVL)_0$	0.024 → 0	0.094 → 0.056	0 → 0.021
	0.011 → 0	0.094 → 0.070	0 → 0.017
	0.011 → 0	0.028 → 0.013	0 → 0.013
$(Piv^-)_0 \cong$			
$(ClPVL)_0$	0.090 → 0	0.094 → 0	0 → 0.067
	0.030 → 0	0.028 → 0.002	0 → 0.028
	0.011 → 0	0.010 → 0.002	0 → 0.0100
$(Piv^-)_0 <$			
$(ClPVL)_0$	0.090 → 0	0.028 → 0.002	0 → 0.032
	0.023 → 0	0.010 → 0	0 → 0.010
	0.045 → 0	0.010 → 0.001	0 → 0.011

[a] $(ClPiv^-)_\infty^\infty = 0$ in all cases.

lactones: cyclization of a β-chlorocarboxylate ion. It was not considered in the study of propiolactone in water[3a] but probably cyclization of β-halopropionate ion proceeds to a much lesser extent and initiation is substantially irreversible.) The new β-lactone can copolymerize, leading to a branch in the chain. Triethylamine causes bulk chloropivalolactone to polymerize;[24] probably few branches are present under these conditions.

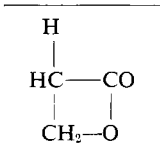
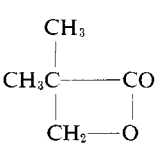
with rate constant 1.4 M^{-1} sec^{-1}. Very recently Parker and coworkers[25] have shown that methyl iodide reacts 2×10^4 faster with tetrabutylammonium acetate in dimethylformamide at 0° than with sodium acetate in formamide at 25°. Such high reactivity may find use as a rapid, mild esterification method.

Analogous dramatic effects of solvent on rate for other anions have been explained by Parker[26] on the basis that in organic solvents the "bare" ion or ion pair reacts, while in water or alcohol, a hydrogen-bonded hydration shell must be pierced by the ion before it can react. In keeping with this idea is the fact that the trialkylammonium and soluble sodium carboxylates are unreactive, owing to a tight hydrogen bond[27] or ion pairing.

$$\overset{+}{R_3NH}\cdots\overset{-}{O}OCR \qquad \overset{+}{Na}\cdots\overset{-}{O}OCR$$

The high value of the rate constant finds perspective in Table VII, where values of the propagation rate constants for various anionic polymerizations are compared. The present reaction is not as fast as most of those in which carbon carries the negative charge, but exceeds those in which oxygen or nitrogen do so and is the fastest anionic ring opening polymerization. The quaternary ammonium carboxylates are the most reactive propagating species which have been isolated

TABLE VI
REACTIVITIES IN ACETONITRILE AND WATER OF CARBOXYLATE IONS

Lactone	Anion	Solvent	Temp, °C	k_I, M^{-1} sec^{-1}	Ref	Ratio
	$\bar{O}OCC(CH_3)_3$	CH_3CN	35	0.42	Present work	10^3
	$\bar{O}OCCH_3$	H_2O	25	3.0×10^{-4}	3a	
	$\bar{O}OCC(CH_3)_3$	CH_3CN	35	0.40	Present work	$>10^2$
	$\bar{O}OCC(CH_3)_3$	H_2O	25	$<4.0 \times 10^{-3}$	Present work	
CH_3I	$\bar{O}OCC(CH_3)_3$	CH_3CN	35	0.89 ± 0.1	Present work	10^4
CH_3Br	$\bar{O}OCCH_3$	H_2O	25	9×10^{-5}	3b	

The observed low effectiveness of chloride ion as initiator, then, does not prove a low value of k_I, because the reverse reaction must be taken into account. This is not the case for fluoride ion; the reaction of α,α-bis(fluoromethyl)propiolactone with tetramethylammonium pivalate gave no ionic fluoride. This lack of reversal contributes to the high reactivity exhibited by fluoride ion.

Magnitude of Rate Constants. The reactivity of the carboxylate ion in acetonitrile is far higher than in water (Table VI). The rate factor is at least 10^2 and may be 10^4 depending on how the comparison is made. High reactivity is also shown toward methyl iodide (equivalent to methyl bromide, the standard compound of Swain and Scott.[3b] Similarly, tetrabutylammonium pivalate at 35° reacted with methyl iodide in THF with rate constant >1.5 M^{-1} sec^{-1} and in benzene

(24) W. L. Jackson, Jr., and J. R. Caldwell, U. S. Patent 3,300,451, to Eastman Kodak Co.

Conclusions

The polymerization of α,α-dialkyl-β-lactones by nucleophiles in organic solvents is consistent with an SN2 reaction at the CH_2 group. The kinetics are second order and the effects of polar and bulky substituents are in accord with this interpretation. The rates of the carboxylate-initiated and -propagated reactions are much higher than those observed in water solution, and are faster than those of other anionic ring-opening polymerizations. Fluoride ion is almost equally effective; chloride ion is much less so, owing in part to reversal of the initiation step with regeneration of β-lactones. This back-reaction also occurs in polymerization of α-chloromethyl propiolactones.

(25) R. Alexander, E. C. F. Ko, A. J. Parker, and J. Broxton, *J. Amer. Chem. Soc.*, **90**, 5049 (1968).
(26) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).
(27) G. M. Barrow and E. A. Yerger, *J. Amer. Chem. Soc.*, **76**, 5211(1954); see, however, S. Bruckenstein and A. Saito, *ibid.*, **87**, 709 (1965).

TABLE VII
COMPARISON OF RATE CONSTANTS OF SOME ANIONIC POLYMERIZATIONS[a]

Propagation reaction	Solvent	Temp, °C	k_P, M^{-1} sec^{-1}	Ref
$S^- + S$	THF	25	65,000	*b*
α-MeS$^-$ + α-MeS	THF	25	830	*c*
S$^-$Na$^+$ + S	THF	25	80	*b*
I$^-$Li$^+$ + I	Heptane	20	0.65	*d*
RCOO$^-$ + α-Me-α-*n*-PrPL	MeCN	35	0.40	Present work
RO$^-$ + EO	DMSO	25	0.13	*e*
I$^-$Li$^+$ + I	THF	30	0.14	*f*
Na$^+$CL$^-$ + N-AcCL	Capro-lactam	25	3.1×10^{-4} (extrap)	*g*
RO$^-$ + EO	Dioxane	70	10^{-4}	*h*

[a] S = styrene, α-MeS = α-methylstyrene, I = isoprene, EO = ethylene oxide, CL = ε-caprolactam. [b] T. Shimomura, K. J. Tolle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89,** 796 (1967). [c] J. Comyn, F. S. Dainton, G. A. Haspell, K. M. Hui, and K. J. Ivin, *Polymer Lett.*, **5,** 965 (1967). [d] H. Sinn and F. Patat, *Angew. Chem. Intern. Ed. Engl.*, **3,** 93 (1964). [e] C. E. H. Bawn, A. Ledwith, and N. R. McFarlane, *Polymer*, **8,** 484 (1967). [f] M. Morton and L. J. Fetter, *J. Polym. Sci., Part A-2*, 3311 (1964). [g] E. Sittler and J. Sebenda, *Coll. Czech. Chem. Commun.*, **33,** 270 (1968); units $^{1/2}$ mol$^{-1/2}$ sec^{-1}. [h] G. Gee, W. C. E. Higginson, K. J. Taylori, and M. W. Trenholme *J. Chem. Soc.*, 4298 (1961).

Experimental Section

Monomers. The dialkyl lactones (Table VIII) were prepared by literature methods,[18,28] usually from bromo acids prepared by nitric acid oxidation of 3-bromopropanols. Pivalolactone was prepared from chloropivalic acid, made by chlorinating pivalic acid. The lactones were distilled from calcium hydride shortly before use and were >99% pure on a 180-cm gc column containing 20% silicone rubber SE 30 on Chromosorb W or on a 120-cm gc column containing 100% didecyl phthalate on Celite. The spirolactone preparations are described in the accompanying paper by Hall, Dence, and Wilson.[29]

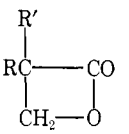
Methyl iodide (Mallinckrodt) was used as received. Acetonitrile (Eastman Organic Chemicals, anhydrous), tetrahydrofuran (Du Pont, purified) dried over sodium, and benzene (Merck) dried over calcium hydride were reagent grade solvents.

Tetraalkylammonium Salts. These were prepared by neutralization of the corresponding quaternary hydroxides by the carboxylic acids in methanol solution, using a pH meter. The solution was evaporated, the residue pumped dry overnight, recrystallized, dried at 42° (0.5 mm) over P_2O_5, and stored at −30° to minimize decomposition. Data are given in Table IX. Melting points are with decomposition. Exposure of hygroscopic salt to atmospheric moisture was avoided as much as possible. The titre of solutions of tetraalkylammonium salts in acetonitrile to perchloric acid in acetic acid did not decrease during a period of several weeks. No corrections for thermal expansion of solvents was made. Attempts to make crystalline pivalate salts of ammonia, *n*-butylamine, diethylamine, and triethylamine failed under these conditions.

Contrary to the report of Vilsmeier[30] the reaction of tetraethylammonium hydroxide with two equivalents of trichloracetic acid gave tetraethylammonium bicarbonate rather than the carbonate. The same compound was prepared by Markowitz' method[31] using the ammonium salt of the anion.

(28) R. Thiebault, N. Fischer, Y. Etienne, and J. Coste, *Ind. Plastiques Mod.* (Paris), **14,** No. 2, 13 (1960).
(29) H. K. Hall, Jr., J. B. Dence, and D. R. Wilson, *Macromolecules*, **2,** 474 (1969).
(30) A. Vilsmeier, German Patent 1,021,854 (1958).

TABLE VIII
β-LACTONE PROPERTIES



R	R′	Bp (mm) or mp, °C	Density, $d^{25}{}_4$[a]
CH_3	CH_3	50 (12)	0.9868 (0.989)
	C_2H_5	63 (16)	0.9753 (0.9746)
	n-C_3H_7	64 (5)	0.9552 (0.9625)
	i-C_3H_7	84 (18)	0.9663
C_2H_5	C_2H_5	49 (2)	0.9715 (0.970)
n-C_4H_9	*n*-C_4H_9	99 (3)	0.9225
C_6H_5	C_6H_5	95	
		75.5 (1)	1.0539
		50 (0.6)	1.0694
C_2H_5	*i*-C_3H_7	93 (18)	0.9665
i-C_3H_7	*i*-C_3H_7	45 (0.30)	0.9638
CH_3	$ClCH_2$	56.5 (1.6)	1.2243
FCH_2	FCH_2	72 (2.2)	1.3380
CH_3	$C_6H_5CH_2$	98 (0.6); 35.5	

[a] Lit.[18] values of densities are in parentheses.

Tetraethylammonium Bicarbonate. Solutions of 65.4 g (0.40 mol) of trichloroacetic acid in 10 ml of water and 42.0 g (0.20 mol) of tetraethylammonium bromide in 20 ml of water were mixed and cooled. The heavy white precipitate was filtered and pressed dry to give 31.2 g of slightly wet solid, then mixed with 46 ml of water and heated with stirring on the steam bath until no more gas was evolved (65 min). The solution was evaporated to dryness on a rotary evaporator and the residue crystallized from ethyl acetate–acetonitrile and dried to give 6.9 g (18.0%) of white crystals.

Anal. Calcd for $C_9H_{21}O_3N$: C, 56.51; H, 11.07; N, 7.32; Cl, 0. Found: C, 56.29, 56.14; H, 10.93, 10.89; N, 7.1, 7.1; Cl, 0.2.

The infrared spectrum showed this to be the bicarbonate, not the carbonate: infrared 2.85 (m), 5.99 (s), 6.23 (s), 6.82 (s), 7.26 (s), 11.98 μ (s).

To a solution of 20.0 g (0.176 mol) of ammonium carbonate (B and A) in 100 ml of water was added 499 ml (0.358 mol) of tetraethylammonium hydroxide (K & K Labs, 0.717 *M*). The solution was evaporated to dryness in a rotary evaporator and pumped overnight. Ethyl acetate, 200 ml, was added to the sticky syrup and, with stirring, acetonitrile until the oil just dissolved. The solution crystallized when left in the freezer at −30°. The solvent was decanted under nitrogen, and the crystals recrystallized by dissolving them in ethyl acetate–acetonitrile with warm filtration through Celite and leaving the solution in the freezer. Filtration under nitrogen and pumping dry over P_2O_5 gave 26.9 g (39.4%) of white crystals. The analytical sample was dried in a pistol at 42° (0.5 mm) over P_2O_5.

Anal. Calcd for $C_9H_{21}O_3N$: C, 56.51; H, 11.07; N, 7.32; Cl, 0. Found: C, 57.35, 57.29; H, 11.00, 11.10; N, 6.7, 6.9; Cl, 0.1.

The infrared spectrum was the same as before.

(31) M. M. Markowitz, *J. Org. Chem.*, **22,** 983 (1957).

TABLE IX
SYNTHESIS OF TETRAALKYLAMMONIUM SALTS

Tetraalkylammonium salt	Recrystzn solvent	Mp (sealed cap.), °C	Yield, %	Calcd, %			Found, %		
				C	H	N	C	H	N
Tetramethylammonium acetate	Acetonitrile	248.0–250.0 dec	85	54.1	11.4	10.5	53.6	11.0	9.9
							53.4	11.0	10.1
Tetramethylammonium benzoate	Acetonitrile–*t*-butyl alcohol	201.0–203.0 dec	78	67.7	8.8	7.2	67.2	8.6	6.6
							67.2	8.5	6.5
Tetraethylammonium pivalate	Benzene	230.0 dec	92	67.5	12.6	6.1	67.4	12.3	5.8
							67.2	12.3	5.7
Tetrabutylammonium benzoate	Hexane–benzene	64.0–67.0	17	76.0	11.4	3.9	76.3	11.2	3.5
							76.1	11.1	3.6
Tetrabutylammonium pivalate	Hexane–benzene	55.0–58.0	73	73.4	13.2	4.1	72.8	13.5	3.9
							72.8	13.5	3.9

β-Chloropivalate Ions. Qualitatively, chloropivalolactone gave a solution with pivalate ion in acetonitrile which gave an instantaneous heavy precipitate with aqueous acidic silver nitrate. Under these conditions chlorolactone, chloro acid, or tetraethylammonium pivalate do not react at all, so the presence of ionic chloride is established.

For Table V, after reaction periods of 10 min, reactions of chloropivalolactone were homogeneous, while those of pivalolactone eventually precipitated in every case. The mixtures were analyzed as follows: for Cl^-, acidified, titrated with $AgNO_3$; for pivalate ion, acidified with oxalic acid, steam distilled, titrated with alkali; for chloropivalate ion, as above; boiled the neutralized solution, cooled, acidified, titrated with $AgNO_3$.

Blank runs showed that Cl^- and pivalate could be determined quantitatively this way. Recovery of chloropivalic acid was 60–70%, but in the event none was found, α,α′-dichloropivalic acid did not distill.

Chloride ion functioned more effectively as initiator when the lactone was present at high concentration. Reaction of 15.00 g of pivalolactone with 0.314 g of tetraethylammonium chloride in 150 ml of refluxing acetonitrile (mole ratio 75) gave 14.7 g of polymer, η 0.26. Excess chloride, 12.43 g, with 7.5 g of pivalolactone in 150 ml of acetonitrile gave a negligible yield of polymer.

Differential Calorimetric Kinetics Method. The half-lives of many of the reactions encountered in this work lay in the 0.5–5-min range, which lying between those measurable by flow methods and by conventional methods, was readily accessible to determination with the differential calorimeter of Lueck, Beste, and Hall.[12] Although convenient, this method is not of highest precision for second-order reactions (where the total area under a curve asymptotically approaching a base line is needed in the calculations.[13] The present work was restricted to homogeneous, nonviscous solutions. This limited us to oligomer formation. The equipment and quantities of reagent have been described[12,13] previously and no further description appears to be required. Steel cells, from which heat leakage is faster than from glass cells, were used sometimes for fast reactions. The solutions were examined carefully after completion of the reaction for any indications of precipitation, or large increase in viscosity, also manifested by failure of the recorder pen to return to the base line. Such runs were discarded, because the heat is assumed to be only that of the chemical reaction, not of differences in stirring.

The data consisted of a trace of the temperature difference as a function of time until the recorder pen returned to the base line (Figure 3). A Bendix model G-15 computer then was used to calculate (A) monomer concentration, (B) the slope $-\mathrm{d} \ln (M)/\mathrm{d}t$, and (C) the integral $(M)\mathrm{d}t$ at each time from the data.

To obtain A, the area under the curve at each time and at infinite time was calculated, and the percentage of reaction calculated as described earlier. This assumes that $\Delta H_I = \Delta H_P$, which is doubtless valid for carboxylate initiators and perhaps for others as well. B was obtained by fitting the ln (M) *vs.* t data with a set of orthogonal polynomial coefficients[32] up to t^3 and differentiating the equation at each time to obtain the slope; C was obtained by conventional methods.

Runs with pivalate ion in acetonitrile gave log (M) *vs.* time plots which were either linear or diverged slightly toward the end (>80% reaction). The drift was assumed to be caused by errors in the determination of total area under the trace, and the initiation ≅ propagation rate constant was taken from the slope of the linear plot. With other carboxylates or F^- in acetonitrile, pronounced curvature occurred. Such runs were analyzed according to Beste and Hall.[17] That method was also used for runs with methyl iodide, and k_P was found to be 0 as required, *i.e.*, simple second-order kinetics held.

"Too slow" means a half-life of >15 min, which, with initiator concentration of 0.1 M, corresponds to k <0.01 M^{-1} sec^{-1}. Of course, such lactones could be studied by conventional methods, because they all do polymerize.

No attempt was made to measure ΔH values for the reactions of nucleophiles with the β-lactones in organic solvents. For water solutions, some values were given recently by Davis, Klimishin, and Carter.[33]

Heats of Combustion. These were determined using a Model 1004-C rotating bomb calorimeter obtained from the Parr Instrument Co. Combustions were carried out by hot-wire ignition in a platinum crucible under 30 atm of oxygen. Time–temperature measurements were obtained with platinum resistance thermometers Model 8160, Leeds and Northrup Co., and a Gaertner Scientific Co. chronograph. A Mueller bridge, L and N No. 9835-B, connected the thermometers to a microvolt amplifier and then to an Azar recorder (L and N). A temperature change of 8×10^{-5} deg could be detected.

Figure 3. Typical differential calorimetric plot; α-methyl-α-*n*-propylpropiolactone initially 0.0222 M; tetraethylammonium pivalate initially 0.0467 M; acetonitrile, 35.0°; right-hand plot is cooling curve (ref 12).

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The jacket temperature was controlled with a Hallikainen Instrument Co. Model 1053A controller.

Combustion measurements were made by accurately defining the initial linear slope of the time–temperature relationship (caused by the difference in temperature between the jacket and bucket temperature), firing the bomb, and obtaining the final linear slope (caused by the heat of rotation of the bomb). These two linear slopes were extrapolated to the ordinate of the midpoint of the bucket temperature rise and thus a corrected temperature difference was obtained from combustion. This value was then corrected for all energy added to the system (fuses, H_2O added to the bomb, specimen holders, energy equivalent of the bomb itself, etc.). Washburn correction and correction for heat capacity of sample (E_c) were made. The resulting energy was then calculated as heat of combustion of the specimen in calories per gram.

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Preparation and Properties of High Molecular Weight, Soluble Oxobenz[*de*]imidazobenzimidazoisoquinoline Ladder Polymer

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ABSTRACT: The synthesis of double chain or ladder polymers from 1,2,4,5-tetraaminobenzene and 1,4,5,8-naphthalenetetracarboxylic acid has been optimized. High ladder polymers of high quality were obtained from the free tetraamine, as well as its hydrochloride salt, in polyphosphoric acid polycondensations at 180°. These ladder polymers were completely soluble in methanesulfonic acid and had intrinsic viscosities ranging from 1 to 6 dl/g. Film-forming and fiber-forming properties were demonstrated. TGA weight losses of less than 10% at 600° in air and less than 5% at 700° in nitrogen were observed. Low-viscosity ladder polymers were obtained from polycondensations in methanesulfonic acid.

Polycondensations of aromatic acids and amines have given rise to several thermally stable polyheterocycles including the conventional polyimides as well as naphthalene imide polymers[1,2] and the polybenzimidazoles as well as tetraazopyrene polymers.[3,4] More recently related ladder polymers referred to as pyrrones,[5–7] BB polymers,[8,9] and polyperimidines[6,10] have been synthesized which are comprised of these same ring systems fused.

Of this group of related polycondensates the ladder types have most recently generated the greatest research interests since they are relatively novel and appear to have potential for applications. Nevertheless due to their complexities, they have not yet been well characterized nor have they yet been developed to any great extent. A primary problem in characterization has been the great difficulty of obtaining high quality linear polymers with reasonably high molecular weights.

One from this group of ladder polymers, the benzimidazobenzophenanthroline-type ladder polymer (BBL), has now been synthesized possessing a combination of properties which appear to be significantly better than the others reported. The synthesis and properties of BBL comprise the subject of this report.

Discussion

From investigations of the polycondensation of aromatic tetraamines and tetraacids or their derivatives, the synthesis of four types of ladder polymers have been studied. Using the currently acceptable structure-based nomenclature[11] these are poly[(10-oxoimidazo[4,-5-*f*]isoindolo[2,1-*a*]benzimidazole-1,2(10H):7,8-tetrayl)-8-carbonyl] (I), poly[(7-oxo-7H,10H-benz[*de*]-imidazo[4′,5′:5,6]benzimidazo[2,1-*a*]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (II), poly[(11-oxoisoindolo-[2,1-*a*]pyrimido[4,5,6-*gh*]perimidine-1,2(11H):8,9-tetrayl)-9-carbonyl] (III), and poly[(13-oxo-1H,-13H-benz[4,5]isoquino[2,1-*a*]pyrimido[4,5,6-*gh*]perimidine-1,2:910-tetrayl)-10-carbonyl] (IV).[12] All possess excellent thermal stability, but in terms of attempting to obtain a high degree of perfection in structure each system differs in its characteristics.

The polymers possessing the perimidine structures (III, IV) are derived from 1,4,5,8-tetraaminonaph-

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