system suitable for mechanistic studies as well as for preparation of block and graft copolymers.

Similar observations of the enhancement of the rate of anionic polymerization of lactones in the presence of cryptates and crown ether have recently been made by Boileau et al.[16]

Acknowledgment. We wish to thank Dr. S. Boileau for making her results on the polymerization of lactones available to us before publication. This work was supported financially by the Polish Academy of Sciences Contract No. 03.1.2.

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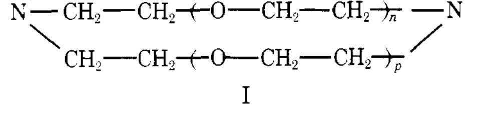
Received September 24, 1975

Use of Cryptates in Anionic Polymerization of Lactones

Macroheterobicyclic ligands such as I which form stable complexes with alkali metal cations[1] called "cryptates" have been recently used in anionic polymerization of vinyl, diene, and heterocyclic compounds.[2] They lead to the formation of complexed ionic species that are highly reactive.

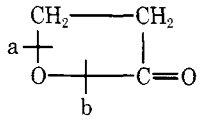


I

$m = n = p = 2$

designated [222]

Extensive studies have been made on anionic ring opening polymerization of β-propiolactone[3-9] and ϵ-caprolactone.[10] There are two modes of cleavage reaction of β-lactones; weak nucleophiles attack the CH_2 group with alkyl–oxygen fission (a), leading to carboxylate end groups, while attack of strong nucleophiles on the carbonyl group causes acyl–oxygen fission (b).



Cleavage of ϵ-caprolactone occurs only at the acyl–oxygen bond (b) and propagation thus proceeds through alkoxide groups. Many side reactions have been found to occur during the propagation when strong nucleophiles are used as catalysts.

We would like to report some preliminary results concerning the use of macrocyclic ligands for the polymerization of β-propiolactone and ϵ-caprolactone.

Monomers. β-Propiolactone (Koch-Light Lab.) was distilled under nitrogen at reduced pressure. The middle fraction was purified over several sodium mirrors in glass apparatus under high vacuum and then stored in the dark at −30 °C, in tubes fitted with break seals. ϵ-Caprolactone (Koch-Light Lab.) which has a high boiling point (bp 65 °C[10] (0.1 mm)) was distilled under nitrogen at reduced pressure and then purified under vacuum in toluene solution over sodium mirrors.

Solvents. Benzene, toluene, and tetrahydrofuran (THF) were purified over calcium hydride and over several potassium and sodium mirrors in glass apparatus sealed under high vacuum.

Initiators. Potassium *tert*-butoxide was prepared under vacuum by reaction of *tert*-butyl alcohol with a potassium mirror. Excess of alcohol was distilled off through a side tube. The potassium salt was then sublimed. Solutions of this salt in THF or toluene were filtered before use. A benzene solution of the dianion of 1,1,4,4-tetraphenylbutane was obtained by stirring a solution of 1,1-diphenylethylene and macrobicyclic ligand over a sodium mirror. This procedure produced rapidly the deeply red colored dianion with the complete disappearance of the sodium mirror. The absorption maximum of the solution is located at about 500 nm. This wavelength corresponds to that found for separated ion pairs and free ions of the sodium salt prepared in hexamethylphosphoramide.[11]

Ligands. The [222] compound was purified by freeze drying in benzene and sealed under high vacuum in tubes fitted with break seals. The same procedure was applied to the freshly redistilled dicyclohexyl-18-crown-6 compound (Aldrich Chemical Co.).

Polymerization. Polymerizations were carried out in glass apparatus sealed under high vacuum. Ligands were added to the catalyst solutions or suspensions just before adding the monomer, except for the benzene solution of the dianion of 1,1,4,4-tetraphenylbutane which cannot be obtained in the absence of [222]. The reaction mixtures were stirred at room temperature. After a period of time polymerization was stopped by addition of a small amount of hydrochloric acid in THF and the polymers were recovered after evaporation of the solvent. Intrinsic viscosities were measured in chloroform at 25 °C for polymers of β-propiolactone and in benzene at 30 °C for those of ϵ-caprolactone. Preliminary polymerization experiments were made in dry toluene or chloroform solution in air (Table I). β-propiolactone was freshly distilled and initiators and the [222] compound were dried before use.

It has been established[2] that a considerable increase in reactivity of anionic initiators can be brought about by complexation of macroheterobicyclic ligands of formula I. Moreover, use of these macrobicyclic compounds permits anionic polymerization of such monomers as styrene, hexamethylcyclotrisiloxane, and episulfides under conditions that ordinarily do not lead to polymers. We have now

Table I
Preliminary Results of Polymerization of β-Propiolactone in Air[a]

Solvent	Initiator	[C], mol l.$^{-1}$ × 10^3	[222], mol l.$^{-1}$ × 10^3	Conversion, %	[η],[b] dl g^{-1}
Toluene	None	0	3.0	0	
	KOH	2.7	0	8.0	
	KOH	2.6_5	3.0	25.0	
	KCNS	2.9	0	0	
	KCNS	2.8	3.0	12.0	0.08
	CH_3COOK	2.7	0	0	
	CH_3COOK	2.7	2.9	7.4	0.10
	KCl	2.7	0	0	
	KCl	2.6	2.9	4.0	
	NaCl	2.6	0	0	
	NaCl	2.6_5	2.8	2.5	
$CHCl_3$	KCNS	2.4	2.6	29.0	0.10
	CH_3COOK	2.6	2.6	17.0	0.46

[a] [M] = 1.22 mol l.$^{-1}$; reaction time = 100 h; room temperature. [b] Measured in $CHCl_3$ at 25 °C.

shown this type of polymerization is effective with β-propiolactone. Preliminary experiments on β-propiolactone performed in air are illustrated in Table I. The data show that [222] increases the yield obtained by initiation with KOH, KCNS, CH_3COOK, KCl, or NaCl in polymerizations in toluene after 100 h at room temperature.

We verified by control experiments in which [222] was used in the absence of added initiator that [222] itself is unable to initiate the polymerization of β-propiolactone or that of ϵ-caprolactone.

In the case of β-propiolactone, polymerization activity depends on the nucleophilicity of the anion. The yield increases in the order KOH > KCNS > CH_3COOK > KCl, that is with a decreasing of the pK_a of the corresponding acid. This has been also observed previously for the bulk polymerization of β-propiolactone at 60 °C initiated by sodium hydroxide, sodium isobutoxide, sodium acetate, and sodium acrylate.[8]

Under the same conditions of polymerization, conversions into poly-β-propiolactone are higher in chloroform than in toluene. This may probably be due to the fact that the polymer formed is soluble in the former solvent whereas it is not in the latter.

The results of some experiments made under high vacuum conditions are given in Table II. Use of macrobicyclic ligands or crown ether compounds markedly increases the rate of polymerization for β-propiolactone. With KOH as initiator in benzene, we obtained a yield of 61% after 2 days with [222] as the ligand and a complete yield after 7 days when the dicyclohexyl-18-crown-6 was used as the ligand (Expt P_1 and P_2). Masuda et al.[13] have found a yield of 48% after 20 days in toluene, at 25 °C, using a KOH concentration 30 times higher and a monomer concentration twice that used by us. Furukawa et al.[14] have obtained a yield of 62% after 14 days at 10–15 °C in toluene, for KOH and monomer concentrations respectively 2500 and 9 times higher than we have used. An increase of the rate of polymerization with the size of the counterion has been reported for various alkali metal acetates used as catalysts for the bulk polymerization of β-propiolactone.[8]

Such an increase of the polymer yield by the addition of macroheterocyclic ligands, in the case of β-propiolactone, may be ascribed both to the increase of the rate of initiation, that is to the increase of the concentration of propagating species, and to the increase of the rate of propagation. A quantitative analysis seems difficult in our systems since they are heterogeneous. Penczek et al.[15] recently studied the kinetics of anionic polymerization of β-propiolactone initiated by sodium acetate in the presence of the complexing crown ether (dibenzo-18-crown-6 ether), in methylene chloride at 35 °C. They found that the apparent bimolecular rate constant of propagation increases not less than 10^2 times when the crown ether is present at a ratio [ligand]/[Na^+] higher than 3.

In the case of ϵ-caprolactone, a few experiments were done using potassium *tert*-butoxide as initiator. Use of [222] in toluene leads to very low molecular weights as can be seen on Table II (P_5). Polymerization of this monomer initiated by sodium alkoxide has been studied by Perret and Skoulios.[10] In addition to high molecular weight polymers, an important amount of very low molecular weight products has been found that might come from intra- and intermolecular transesterifications giving cyclic compounds. These side reactions occur to a higher extent in THF than in toluene because ionization of alkoxides is more pronounced in the former solvent. We verified that alkoxides react with the ester groups of the chains by adding potassium *tert*-butoxide to a solution of poly-ϵ-caprolactone (200 mg of polymer in 15 ml of THF). The initial intrinsic viscosity of the polymer was 2.42 dl g^{-1} in benzene at 30 °C. It falls to 0.05 dl g^{-1} after reaction with potassium *tert*-butoxide (3 × 10^{-4} mol) during a few minutes at room temperature. Potassium alkoxide end groups complexed with a macroheterobicyclic ligand are highly reactive with the ester groups in monomer and polymer, and we did not

Table II
Anionic Polymerization of Lactones with Complexed Cations as Counterions at Room Temperature

Expt	Monomer ([M], mol l.$^{-1}$)	Catalyst ([C], mol l.$^{-1}$)	Solvent	[ligand][a]/[M^+]	Conversion, %	[η],[b] dl g^{-1}	M_V[c]
P_1	βPL (1.4)	KOH (1.0×10^{-3})	Benzene	2.0	61 after 24 h	0.65	
P_2	βPL (1.3)	KOH (9.6×10^{-4})	Benzene	1.0	100 after 7 days	2.60	
P_3	βPL	$Na^{+-}DD^-Na^+$ (8.0×10^{-5})	Benzene	>1	21 after 8 days		
P_4	ϵCL (0.6)	*t*-BuOK (5.3×10^{-4})	THF	0	97 after 1.30 h	57% white powder, [η] = 0.82 43% oil, [η] = 0.03	66 000 1 000
P_5	ϵCL (0.4)	*t*-BuOK (7.2×10^{-4})	Toluene	1.1	93 after 8 days	Oil, [η] = 0.06	2 500
P_6[d]	ϵCL (0.8)	*t*-BuOK (6.4×10^{-4})	THF	1.2	13 after 15 min	64% white powder, [η] = 0.71 36% oil, [η] = 0.03	50 000 1 000

[a] Ligand: [222] for P_1, P_3, P_5, and P_6; dicyclohexyl-18-crown-6 for P_2. [b] Intrinsic viscosities measured in $CHCl_3$ at 25 °C for P_1 and P_2; in C_6H_6 at 30 °C for P_3–P_6. [c] M_V calculated from: $[\eta] = 9.94 \times 10^{-5} M_V^{0.82}$.[12] [d] Polymerization carried out at −50 °C.

obtain high molecular weights in toluene at room temperature. An experiment was carried out at −50 °C in THF (P_6). At this temperature, we observed a precipitation of the poly-ϵ-caprolactone and the proportion of low molecular weights is nearly the same as for a similar experiment made at room temperature with uncomplexed potassium *tert*-butoxide (P_4).

In conclusion, it has been shown that the addition of macrocyclic ligands leads to an increase of the reactivity of ionic species for the anionic polymerization of lactones. Use of such complexing agents for cations allows the initiation of β-propiolactone polymerization with weak nucleophiles under conditions that ordinarily do not lead to polymers. Anionic polymerization of ϵ-caprolactone in the homogeneous phase with macrobicyclic ligands leads to a higher proportion of oligomers than in the case of uncomplexed species. This is due to the enhancement of the reactivity of alkoxide end groups with cryptates as counterions. This effect is less pronounced for polymerizations occurring in the heterogeneous phase, for example, for ϵ-caprolactone polymerization at −50 °C.

Acknowledgments. We wish to thank Professor Penczek for sending us his results on the polymerization of lactones before publication. This work has been supported by the "Société Nationale des Poudres et Explosifs" through Grant No. 21/72/D

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Received October 13, 1975

Block and Graft Copolymers of Pivalolactone. I. A New Class of Elastoplastics and Thermoplastic Elastomers

The forced union, by block and graft copolymerization of unlike polymeric segments can lead to controlled phase separation often yielding compositions with unusual and useful properties. In particular, when one of the components is elastomeric and forms a continuous phase, then separation of a glassy or crystalline component can develop tiepoint domains connecting elastomeric chains so that the resulting network exhibits the properties of a cured elastomer. Commercially important block polymers of this type offering thermoplastic processability include poly(styrene-*b*-butadiene-*b*-styrene) and the isoprene analogue, segmented polyether esters and polyether or polyester urethanes.

We wish to report on an unusual class of copolymers in which grafted blocks of polypivalolactone combine, undergo phase separation, and rapidly form highly crystalline tiepoint domains. These compositions, stable in the melt and solvent resistant, are striking examples of thermoplastic elastomers that are readily prepared.

The facile ring-opening polymerization of pivalolactone (PVL, 2,2-dimethyl propiolactone) is well known and has been recently reviewed[1] as have homopolymer properties.[2–4] Publications dealing with grafts of the type described here have, with perhaps one exception,[5] appeared only in the patent literature.[6–11] Graft polymerization of pivalolactone is readily initiated by carbanion,[7] oxyanion,[5] and in particular carboxylate[6,8,9,11] sites randomly located on the base polymer backbone. Even tertiary amine sites can initiate by reacting with monomer to form a zwitterion.[11,12] Carboxylate anions with bulky organic counterions, such as tetrabutylammonium, which form loose ion pairs in solvating solvents such as tetrahydrofuran, are sites favored for rapid initiation and propagation. The grafted chains are "living" in that the propagating group, the carboxylate anion, is quite stable in the system, undergoes no common termination reaction, and does not participate in chain transfer to monomer.[1] It can, however, transfer its activity to any available carboxyl group by simply accepting the proton.

Experimental Section

For grafting the base polymer is dissolved in tetrahydrofuran and stirred under gentle reflux. The carboxylate anion sites are developed by reaction of carboxyl containing polymers with 20–100% of the theoretical amount of tetrabutylammonium hydroxide, normally handled as a 1.0 M solution in methanol. The adequacy of partial neutralization and the distribution of pivalolactone units over all available carboxyl groups has been demonstrated by the similarity in melting behavior of graft products prepared with neutralization levels from 2 to 100%. In copolymers containing pendant ester groups the amount of base determines by saponification (1 h at reflux) the number of carboxylate ion sites. Cyclic anhydride functionality reacts rapidly, even with less than stoichiometric amounts of alcoholic base, to give the half ester initiating site.

Pivalolactone, purified by passage through a short column of neutral alumina, is added slowly enough to control the exotherm. An additional 30–60 min of heating completes the reaction, and at high modification levels the usually clear solution may gel. The system is normally acidified with 12 M HCl and the product precipitated by addition to water, ethanol, or acetone. Conversions are normally quantitative, with 95–100% of the grafted monomer recovered in the yield of the graft copolymer. For example, 50 g of pivalolactone reacted with 200 g of a base resin normally yields 247–250 g of grafted product. Homopolypivalolactone is either absent or present at low levels.

Graft polymerizations can also be carried out in the molten polymer, when it is low melting and has some degree of polarity. Further discussion of this special case will appear in a later publication.

Unpublished work at Haskell Laboratory, E. I. du Pont de Nemours and Co., has shown that pivalolactone caused skin tumors in mice when applied as a 25% solution in acetone for most of the life span of the mice. The time required for tumor formation was greater than that for β-propiolactone, a positive control in the test, and the extent of tumor formation was much less than for β-propiolactone.