

PREPARATION, STRUCTURE AND PROPERTIES OF POLYESTERS FROM SUBSTITUTED β -LACTONES

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ABSTRACT

The anionic polymerization reactions of a series of α,α -disubstituted- β -propiolactones were investigated for the effect of the α -substituents and reaction conditions on the rate and mechanism of the propagation reactions and for the effect of polymer structure on physical properties, especially on crystalline properties. An unexpected, apparent steric acceleration was observed in the rate studies, and all polymers, even those prepared from racemic mixture of chiral monomers, were found to be crystalline with melting points having an unexplicable, direct relationship with the size ratio of the two α -substituents. The preparation and properties of a new polymer, poly- α -methylene- β -propiolactone, is also reported.

INTRODUCTION

The anionic polymerization of α -disubstituted- β -propiolactones has been a subject of interest for many years, formerly because of the potential practical importance of polypivalolactone as a fiber, and recently for graft and block copolymers based on polypivalolactone as the "hard" segment in thermoelastomers (1)(2). The principal basis for these interests lies in the fact that the polyester from pivalolactone is highly crystalline with a high melting point (3), and also pivalolactone itself (α,α -dimethyl- β -propiolactone) can be readily prepared by a number of practical synthetic routes. Furthermore, the anionic polymerization of pivalolactone is a "living polymer" system and can readily be applied to the preparation of block and graft copolymers because the reaction is initiated by carboxylate salts as shown in Figure 1 (4)(5).

Early investigations on the anionic polymerization reactions of β -lactone monomers containing two different α -substituents were carried out by: (a) Fischer and coworkers in 1962, who reported on the melting points of their polymers (6); (b) by Hall in 1969, who studied their rates of initiation for polymerization reactions initiated by ammonium carboxylates in various solvents (7); and (c) by Lenz and coworkers in 1973, who studied the "living polymer" characteristics of these monomers and prepared elastomeric ABA block copolymers with polypivalolactone segments as the A blocks (5).

Since these latter investigations on the preparation and properties of block copolymers, this laboratory has been interested in a variety of aspects of the synthesis-structure-property relationships of polyesters from the α,α -disubstituted- β -propiolactones, particularly, with: (a) rate investigations to study the effects of α -substituents, reaction solvents, and reaction homogeneity on the kinetics and mechanisms of their anionic polymerization reactions, and with: (b) a study of polymer crystalline properties as a function of polymer stereoregularity and substituent size ratio.

ANIONIC POLYMERIZATION MECHANISM

It is now accepted that the propagation mechanism in the anionic polymerization of α,α -disubstituted- β -propiolactones is an S_N2 reaction in which the lactone ring is opened at the β -carbon-oxygen bond and the active endgroup is a carboxylate anion ion pair as shown in Figure 1. Kinetic investigations in this laboratory have revealed unusual and unexpected effects of the size of the α -substituent on the global or average propagation rate constants. It was found that with increasing substituent size, for *n*-alkyl α -substituents, an unexplained steric acceleration of the propagation rate occurred (8)(9). Also unexpected was the observation that the rate constant was higher in THF than in the more polar reaction solvent DMSO (8)(10).

Substituent effects

The apparent steric acceleration of the propagation reaction by increasingly larger *n*-alkyl substituents in the α -position of β -propiolactone is shown by the data in Table 1 (8)(11). Within the series in which one of the α -substituents is the methyl group, the average propagation rate constant was observed to increase by 5 to 10 percent with each incremental increase in the length of the *n*-alkyl group, which was present as the second α -substituent. As seen in Table 1, this increase in rate constant was associated with an increase in activation energy, which, however, was offset by an increase in activation entropy. Hence, the observed steric acceleration is clearly an entropy effect, which offsets the expected deactivation normally seen in such reactions with increasing substituent size and which is generally attributed to either steric hindrance to attack or increased ring stability.

This pattern did not persist, however, when one of the two α -substituents was the *n*-butyl group and the second one was increased in size from the methyl to the ethyl group, as seen in Table 1. In that case, the average propagation rate constant decreased, although a

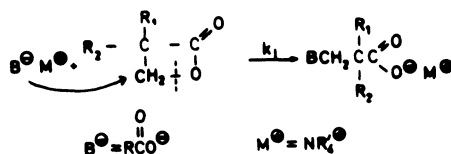
TABLE 1. Average propagation rate constants for the anionic polymerization of α, α -disubstituted- β -propiolactones

α -Substituents		k_p (a) $M^{-1} \text{ min}^{-1}$	Activation Parameters	
R_1	R_2		ΔE^* , kcal M^{-1}	ΔS^* e.u.
CH ₃	CH ₃	10.2	-	-
CH ₃	C ₂ H ₅	11.2	6.4	-42.3
CH ₃	<i>n</i> -C ₃ H ₇	11.8	6.6	-41.5
CH ₃	<i>n</i> -C ₄ H ₉	13.0	6.9	-40.3
C ₂ H ₅	<i>n</i> -C ₄ H ₉	9.5 ^(b)	7.5	-39.8

(a) In dimethyl sulfoxide solution at 22°C with tetraethylammonium counterion.

(b) At 30°C.

Initiation



Propagation

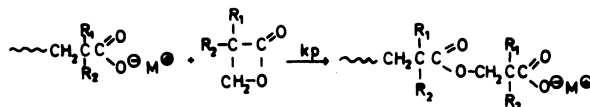


Figure 1. Initiation and propagation mechanisms in the anionic polymerization of α, α -disubstituted- β -propiolactones.

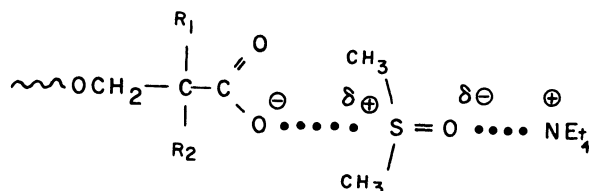


Figure 2. Anion solvation of active end groups by DMSO.

increase in activation entropy was again observed, but this time it was not sufficient to offset the increase in activation energy. The molecular or mechanistic basis for these changes in the activation parameters with substituent size remains open to question and is under further study.

Solvent effects

The selection of the reaction solvent can play a very important role in the course of these polymerization reactions. In the rate studies referred to above, as mentioned, it was observed that for two different aprotic solvents, DMSO and THF, the propagation rate constant was higher in the solvent of lower polarity, THF. This difference was attributed to the importance of anion solvation in this reaction (8)(10), as illustrated in Figure 2, but other explanations are possible, and such solvent effects are now under further investigation in this laboratory.

Living polymer character

Early investigations in this laboratory demonstrated from molecular weight and molecular weight distribution determinations that these reactions involved "living polymers" systems, with no termination or transfer (5). Very recently we have observed, with a series of α, α -disubstituted- β -propiolactone monomers, that when the growing polymers precipitated during polymerization these living-polymer characteristics were maintained and a narrow molecular weight distribution resulted, but when the growing polymers formed an immobile gel, the reaction rate slowed down and a bimodal or multiple peak molecular weight distribution was formed (11). Both precipitation and gelation were probably caused by crystallization of the growing polymer from the reaction solution, but it was surprising that only the latter (gelation) resulted in an apparent reduction in the reactivity of the living end groups. These observations are under further investigation.

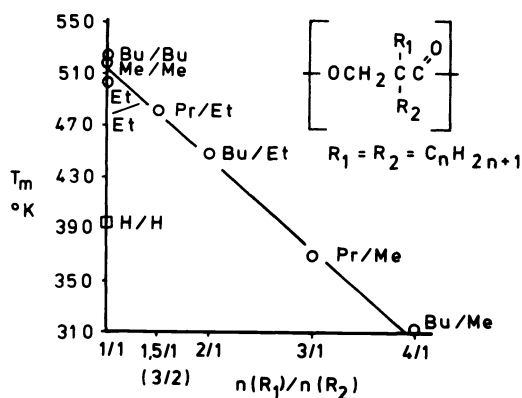


Figure 3. Relationship between polymer melting points, T_m , and the ratios of sizes of the two α -substituents, according to the number of carbon atoms in each, in poly- α, α -disubstituted- β -propiolactones.

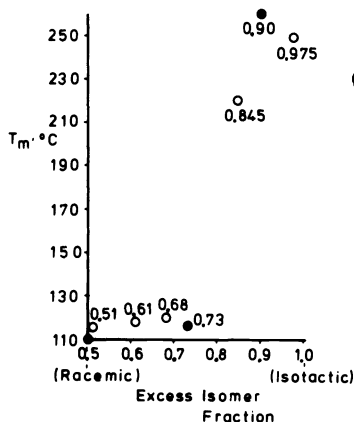
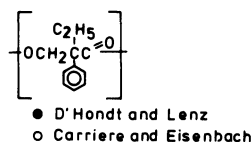
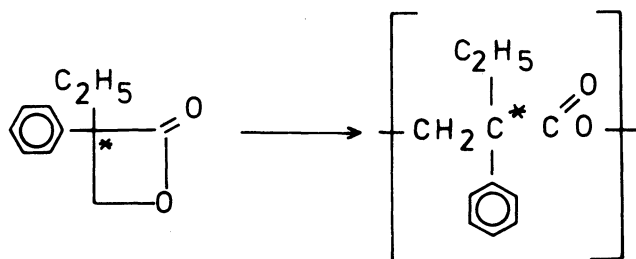


Figure 4. Relationship between polymer melting point, T_m , and tacticity in poly- α -ethyl- α -phenyl- β -propiolactone.

POLYMER CRYSTALLINE PROPERTIES

The results of crystallinity and melting point studies were equally surprising. All polymers prepared from monomers with two different α -substituents were crystalline, even though the monomer was chiral and racemic mixtures of the two isomers were polymerized in a homogeneous reaction medium (12). Furthermore, the polymers were found to show an unaccountable linear relationship between substituent size ratio and melting point, as shown in Figure 3 (12). Also it was demonstrated in our early investigations (5)(13), and has been investigated in much greater detail recently by R. Prud'homme and co-workers (14) that most or all of the polymers in this series can exist within the crystalline phase in either of two conformational forms: a helical form or a planar zig-zag form. We were able to show that the former could be converted to the latter by mechanical straining (13), and this type of mechanically-induced crystal-crystal interchange may be responsible for the lack of acceptance of polypivalolactone as a textile fiber.

Our investigations (15), as well as more recent ones by Eisenbach and Carrier, on the crystalline properties of polymers prepared from a racemic monomer compared to those prepared from an optically-active monomer, indicated that the crystal structures of the racemic and optically active, or isotactic polymers were quite different. The results of these investigations for the variation of polymer melting point with tacticity in the polymerization of α -ethyl- α -phenyl- β -propiolactone, as shown below, are collected in Figure 4:



The data in Figure 3 suggest that there are two populations of crystalline states as a function of tacticity, with a change in crystal structure occurring in the region of 70-80% isotactic dyad content. These results are supported by wide angle x-ray diffraction studies on this polymer which conclusively reveal the presence of two different crystal lattices (15).

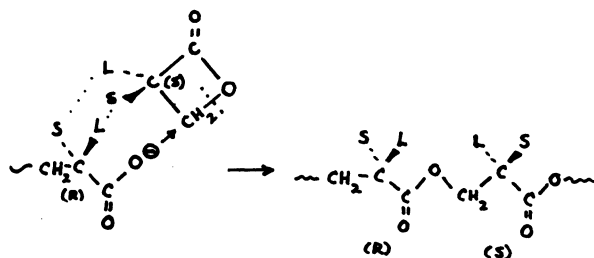


Figure 5. Steric interactions favoring syndiotactic placement in the anionic polymerization of α,α -disubstituted- β -propiolactones.

Recent investigations in the laboratory of N. Spassky on the preparation of optically-active polymers by the stereoselective polymerization of other racemic monomers in this series have given similar results and have also been successful in determining polymer tacticity by NMR analysis (17)(18). However, it is still uncertain as to why the normal racemic polymers are crystalline, and an earlier suggestion from our laboratory that a kinetic selectivity in the propagation reaction leads to a syndiotactic polymer remains unproven. The basis for the proposed kinetic selectivity is the possibility of a lower steric hindrance to attack when a carboxylate anion on an end group unit having one type of chirality attacks a monomer of the opposite chirality, as shown in Figure 5. Furthermore, a syndiotactic-type of stereoregularity has been suggested for the crystalline regions in the racemic α -methyl- α -propyl- β -propiolactone polymer by crystal structure determinations (19), but the NMR results indicate that the racemic polymer contains equal contents of syndiotactic and isotactic dyads (17)(18).

POLY- α -METHYLENE- β -PROPIOLACTONE

Recent investigations in this laboratory have also been concerned with the preparation, polymerization and polymer property investigations on a new monomer in this series: α -methylene- β -propiolactone. This monomer is readily prepared, but very difficult to isolate, by the base-catalyzed cyclization of α -bromomethylacrylic acid, as shown in Figure 6 (20). The conditions for cyclization also lead directly to the anionic polymerization of the lactone.

Poly- α -methylene- β -propiolactone is highly crystalline, and polymer melting points as high as 265°C have been observed depending on molecular weight and annealing conditions (20). Additional investigations on monomer and polymer preparation and polymer properties are presently in progress.

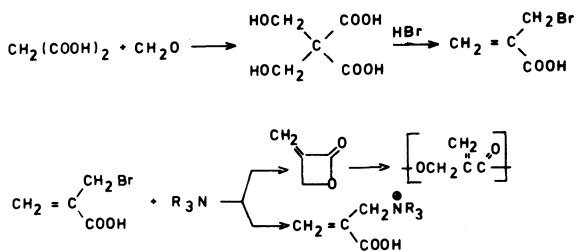


Figure 6. Preparation and polymerization of α -bromoacrylic acid to poly- α -methylene- β -propiolactone.

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