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Racemic Poly(α-Alkyl-α-Phenyl-β-Propiolactone) Substituent Dependence

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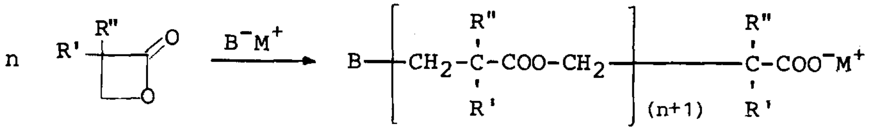
SUMMARY

The α-phenyl-α-alkyl-β-propiolactones (alkyl groups = $-CH_2CH_3$; $-CH_2CH_2CH_3$; $-CH_2CH_2CH_2CH_3$) were synthesized and polymerized by anionic ring-opening polymerization by tetraethylammonium benzoate (non-chiralic initiator). It was found that the molecular weight of polylactones increased as the size of the alkyl substituent increased. Poly(α-propyl-α-phenyl-β-propiolactone) showed the highest melting temperature. Lactones polymerized using tetraethylammonium dibenzoiltartrate (chiralic initiator) gave polyesters with higher melting temperature than those obtained with a non-chiralic initiator under the same conditions.

INTRODUCTION

The anionic polymerization of α,α-disubstituted β-lactones has been investigated by various authors (HALL (1969), LENZ (1974), EISENBACH and LENZ (1976), BIGDELI and LENZ (1978), CARRIERE and EISENBACH (1981).



The resulting polyesters are more or less crystalline depending of the α-substituents of the β-lactones (CORNIBERT et al. (1973), LENZ (1974), D'HONT and LENZ (1978), MARCHESSAULT et al. (1978), ALLEGREZZA et al. (1978), CARRIERE and EISENBACH (1981).

This work concerns the effect of the alkyl substituent of the different poly(α-phenyl-α-alkyl-β-propiolactones) obtained with chiral and non-chiral anionic initiators on the melting temperature of the polymer. The influence of the polymerization temperature on this parameter and on the molecular weight has also been studied.

EXPERIMENTAL PART

Various racemic β-propiolactones have been obtained from benzyl cyanide and ethyl carbonate in a general five-step

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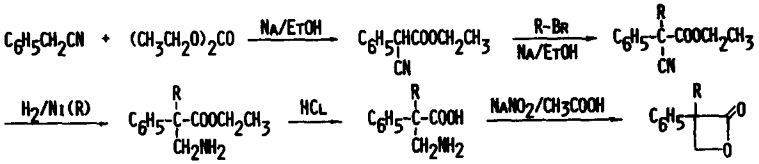
sequence by TESTA et al. (1958a,b,c,d):



The final products were already reported by TESTA et al. (1958a). Here we caracterized these compounds by proton nmr spectroscopy (60-MHz, Varian T-60-A).

α-ethyl-α-phenyl-β-propiolactone. bp. = 85°C (0.25 mm) ; nmr (neat): 0.90 ppm (t,3H,CH_3); 2.00 ppm (c,2H,CH_2); 4,40 ppm (s,2H,CH_2-ring) and 7.38 ppm (s,5H,C_6H_5).

α-propyl-α-phenyl-β-propiolactone. bp. = 95°C (0,1 mm) ; nmr (neat): 0.85 ppm (t,3H,CH_3); 1,25 ppm (m,2H,CH_2); 1,95 ppm (t,2H,CH_2); 4.42 ppm (s,2H,CH_2-ring) and 7,40 ppm (s,5H,C_6H_5).

α-butyl-α-phenyl-β-propiolactone. bp. = 115°C (0,2 mm); nmr (neat): 0.80 ppm (t,3H,CH_3); 1,23 ppm (m,4H,CH_2CH_2); 2,00 ppm (t,2H,CH_2); 4.50 ppm (s,2H,CH_2-ring) and 7,42 ppm (s,5H,C_6H_5).

Anionic Initiators

Tetraethylammonium benzoate (TEAB) and tetraethylammonium dibenzoiltartrate (TEADBT) were synthetized by ROBERTS et al. (1951). The initiator were dried under vacuum over P_2O_5 at 40°C. Both hygroscopic salts were stored over P_2O_5.

Anionic polymerization

These polymerizations were performed in closed flasks under nitrogen, at constant temperature using THF as solvent. The polymer solution was precipitated and re-precipitated with ethanol. The product was dried at 40°C until reaching constant weight.

Fractions of polymer at different polymerization times were obtained precipitating aliquots of the initial polymer solution. (Polym. 1 to 4).

Polymer thermograms were run in a Differential Scanning Calorimeter Perkin-Elmer Model DSC-2.

RESULTS AND DISCUSSION

The conditions of polymerization and the parameter which characterize the different poly-(α-alkyl-α-phenyl-β-propiolactones) are summarized in Table I.

Table I (Polym. 1 to 4) shows that the $\bar{M}$n of the lactones increases with the polymerization time as it was expected. Besides, it is also observed that for the poly(α-phenyl-α-propyl-β-propiolactone) and for the poly(α-phenyl-α-butyl-β-propiolactone), the melting temperature is independent of the polymerization time. This is shown in the thermograms of Figures 1 and 2.

TABLE I

Polymerization of α-alkyl-α-phenyl-β-propiolactones

Polym. Nº	alkyl group	initiator	Polymer Temp. (°C)	Polymer Time (h)	Melting Temp. (°K)	$\bar{M}n$	$\bar{P}n$
1	propyl	TEADBT	60	2	499,6	2800	15
2	propyl	TEADBT	60	4	499,1	4200	22
3	propyl	TEADBT	60	19	498,6	4500	24
4	propyl	TEADBT	60	115	499,1	7800	41
5	ethyl	TEAB	18	720	375,8	2700	15
6	propyl	TEAB	18	720	485,6	5600	29
7	butyl	TEAB	18	720	458,9	7200	35
8	butyl	TEADBT	43	48	512,6	--	--
9	butyl	TEADBT	43	96	512,4	--	--
10	butyl	TEAB	43	48	487,6	3200	16
11	butyl	TEAB	43	96	487,6	--	--

conversion: 30-89%

Figure 1 shows that some thermograms of the poly(α-phenyl-α-propyl-β-propiolactone) exhibit more than one endotherm. This has also been observed in other types of polymers, as well as in the polypropiolactones (ROBERTS (1970); BORRI and BRUCKNER (1971)). It has also been observed that the endotherm at lower temperature disappears with increasing polymerization time, i.e. with increasing chain length.

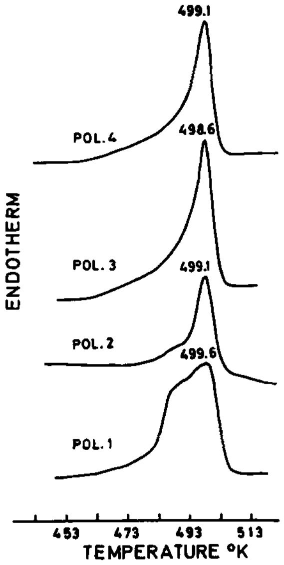


Fig. 1. DSC of poly(α-phenyl-α-propyl-β-propiolactones)*

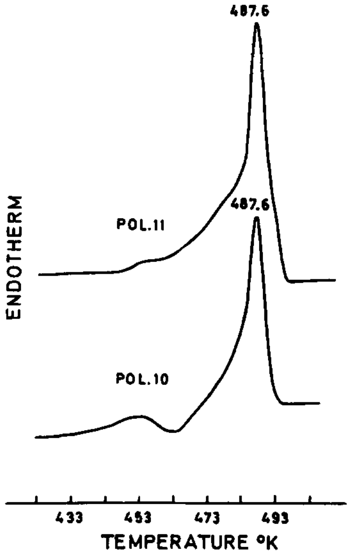


Fig. 2. DSC of poly(α-butyl-α-phenyl-β-propiolactones)**

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*) Lactone: 23,63 mmol, Initiator: 0,310 mmol in 50 ml of THF

**) Lactone: 2,57 mmol, Initiator: 0,032 mmol in 10 ml of THF

The peak at lower temperature can be attributed to crystallites former by not folded short chains.The one at higher temperature corresponds to more perfect crystallites of a folded chain former by polymer of long chains. As the polymerization time increases the chain length also increases and therefore the ratio of folded crystallites is also enhanced. Due to the fact that the maximum of the higher melting endotherm does not vary with the polymerization time, it can be concluded that the packing of chains in higher crystallites is independent of chain length.

The alkyl substituent of polylactones influences the melting temperature, as shown in Figure 3.

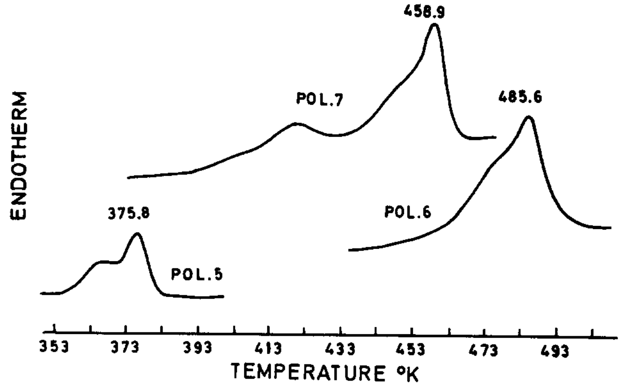

Fig.3 . DSC of poly(α-alkyl-α-phenyl-β-propiolactones)

The poly(α-phenyl-α-propyl-β-propiolactone) is the highest melting of the three polylactones. The melting temperature of poly(α-butyl-α-phenyl-β-propiolactone) is lower than that of poly(α-propyl-α-phenyl-β-propiolactone) may be due to the fact that the packing of the macromolecules in the former is more sterically limited than in the latter due to the greater volume of the substituent group.

The data in Table I (polym. 8 and 10; 9 and 11) show that polypropiolactones obtained with TEADBT melt higher than the ones obtained with TEAB under the same conditions.

This behavior can be attributed to the fact that the optically active initiator exerts a certain control on the addition of the racemic monomeric mixture during the growth step producing polymers with a higher degree of tacticity.

To determine the effect observed of a preferential incorporation of the enantiomeric lactones (stereoblock) by the TEADBT chiralic centre, the optical activity of low molecular weight polylactones (Polym. 1 to 4) was determined.

None of the polylactones showed optical activity, even the ones of lower molecular weight. This fact indicates that there is no preferential incorporation of one of the enantiomers, and therefore the higher tacticity grade of the polymer could be due to an alternate disposition of both enantiomeric lactones in the polymer chain.

Finally, Table I shows that as $\bar{M}n$ increases with the number of carbons of alkyl group in the C_{α} of the polylactone. BIDGELI and LENZ (1978) found a similarity between the polymerization rate and the length of the alkyl substituent in polylactones. These facts may be explained by assuming that during the propagation hydrophobic interaction occurs between the alkyl substituent of the macroanion and the substituent of the monomer in a polar solvent. This would increase the local concentration of monomers and active centres. Thus the greater the length of the alkyl group, the greater is the hydrophobic interaction and therefore propagation would be faster and the $\bar{M}n$ higher.

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