Journal of Thermal Analysis, Vol. 38 (1992) 303-311

(RS)-, (R)- AND (S)-3-BENZYL-3-ETHYL 2-OXETANONE POLYMERIZATION WITH CHIRAL AND ACHIRAL INITIATORS

III. DSC study of the thermal properties of the resulting polyesters

F. J. Carrière and R. Blottiau*

LABORATOIRE DE CHIMIE MACROMOLECULAIRE, UA 24, UNIVERSITE PIERRE ET MARIE CURIE, TOUR 44, 4 PLACE JUSSIEU, 72252 PARIS CEDEX 05, FRANCE

The polymerization of 3-benzyl-3-ethyl 2-oxetanones leads to three types of polymers: poly *RS* (enantiomer excess, $ee = 0$), poly *R* or poly *S* (*Ree* > *See*) and polyracemate. All these polymers are crystalline and the thermal properties (T_g, melting T_M and ΔH_M) depend mainly on the *ee* of the polymer. The propagation of the polymerization is not stereospecific. The use of heating-cooling cycles leads to a pure crystalline form melting at the highest temperature. The polyracemate has the behaviour of a pure polymer which melts at a lower temperature, a prolonged heating in the melt induces a strong racemization.

Keywords: DSC, polyester, polymerization

Introduction

(RS)-, (R)- and (S)-3,3-disubstituted 2-oxetanones (b-lactones) – with ethyl, phenyl [1] and benzyl, ethyl [2] as substituents – have been polymerized with achiral or (RS) and (S) chiral initiators being either tetraal- kylammonium carboxylate or nickel(II) carboxylate complexed by tributyl phosphine [3]. In both cases, the chirality was given by the carboxylic acid moiety. The anionic polymerization of 3,3-disubstituted 2-oxetanones leads to crystalline polymers even when a racemic β-lactone carrying two different bulky substituents is polymerized [4]. In addition, it has been shown that these polymerizations are not stereospecific [5] and

---

* Author to whom correspondance should be addressed.

that the polymers obtained from racemic monomers have a very low stereoregularity [6]. A kinetic study of polymerization of 3-benzyl-3-ethyl 2-oxetanones (BzEO) shows that initiation alone is more or less stereospecific [7].

In this article, we shall describe a DSC study of the resulting polymers to try to have a better approach either on the stereoregularity of the polymers or on the influence of the initiator chirality on the stereoregularity during the BzEO polymerization.

Experimental

1 – Thermal measurements

The thermal measurements were carried out with a DSC 7 Perkin-Elmer apparatus with 2 to 5 mg of sample in sealed aluminium pans. The apparatus was calibrated with standards, indium and zinc, as well for temperatures as for energy (ΔH). We shall define T_M as the temperature of the maximum of the melting peak and ΔH_M as the variation of the enthalpy of melting (in J/g) between the starting of the peak T_1 and the end of the peak T_2 (return to baseline). T_m is the onset defined as the intersection of the extrapolated baseline with the tangent drawn on the leading edge of the peak. This point was determined graphically.

– 1st PAS: first melting of a sample without thermal history

– 2nd PAS: second melting, after 1st PAS the samples were cooled slowly (20 deg/min) and reheated to melting (20 deg/min).

– Heating-cooling cycles [8, 9]: They were carried out with a gap of temperature of about 50°C, T_{max} was around the first then the second melting maximum with a rate of 20 deg/min.

– Polyracemate was prepared by dissolving equal quantities of poly *R* and poly *S* in $CHCl_3$ and the solvent was evaporated.

2 – Polymerization

The technique of polymerization [1, 2] and the synthesis of BzEO [2] were previously described.

Results and discussion

The results of melting (1st PAS and 2nd PAS) are collected in Table 1.

Table 1 T_M, ΔH_M and T_g values of RS, R and S polymers obtained with an achiral initiator, without thermal history (1st PAS) and cooled slowly (2nd PAS)

		2a initiator[c]			
Polymer	Melting	Melting		Glass transition	
		$T_M/^\circ C$	$\Delta H_M / J \cdot g^{-1}$	$T_g/^\circ C$	$\Delta H / J \cdot g^{-1} deg^{-1}$
S	1st PAS[a]	219.6	26.1	76.0	0.27
S	2nd PAS[b]	219.2	20.0	72.4	0.47
R	1st PAS	231.0	33.0	76.4	0.21
R	2nd PAS	230.0	30.0	74.0	0.13
RS	1st PAS	147.0	23.5	65.0	0.28
RS	2nd PAS	–	–	70.2	0.85

a- 1st PAS: first melting, b- 2nd PAS: second melting, heating and cooling rate: 20 deg/min, c- 2a initiator: NBu_4 acetate

Table 2 T_M, ΔH_M and T_g values of R, S and RS polymers obtained with a chiral initiator, polymers without thermal history (1st PAS) and cooled slowly (2nd PAS)

		2c initiator[c]			
Polymer	Melting	Melting		Glass transition	
		$T_M/^\circ C$	$\Delta H_M / J \cdot g^{-1}$	$T_g/^\circ C$	$\Delta H / J \cdot g^{-1} deg^{-1}$
S	1st PAS[a]	219.6	29.5	79.0	0.31
S	2nd PAS[b]	219.2	22.0	72.0	0.58
R	1st PAS	230.0	37.0	78.0	0.23
R	2nd PAS	231.0	33.7	68.0	0.55
RS	1st PAS	147.5	24.0	76.4	0.36
RS	2nd PAS	–	–	70.0	1.10

a- 1st PAS: first melting, b- 2nd PAS: second melting, heating and cooling rate: 20 deg/min c- 2c initiator: NBu_4 (S)-2-methylbutyrate

The results of Tables 1 and 2 show that:

i) The racemic polymer (poly *RS*) melts 72 to 84°C lower than poly *S* and poly *R*, respectively. For ΔH_M values, the differences are a little less important; ΔH_M varies from 23.5 (poly *RS*) to 26.1 (poly *S*) and 33.0 J/g (poly *R*).

ii) The values of T_M as well as of ΔH_M depend essentially on the optical purity (i.e. enantiomeric excess, *ee*) of the starting monomer. A highest *ee* has been obtained for *R* monomer, which gives $T_M=231.0^\circ$C and $\Delta H_M=33.0$ J/g for poly *R* and $T_M=219.6^\circ$C and $\Delta H_M=26.1$ J/g for poly *S* (achiral initiator).

iii) There are no differences for T_M values in the three cases, which ever is the initiator.

iv) A poly *RS* does not crystallize on cooling and therefore has no second melting peak, which involves a very low stereoregularity of the polymer chain.

v) For a second melting, T_M values do not shift, on the contrary ΔH_M reduced by 23% (poly *S*) and by 9% (poly *R*). The less important decrease is the higher *ee*, which involves a higher stereoregularity of poly *R* chain.

As far as the stereoselection of the polymerization is concerned, the comparison of the results of Tables 1 and 2 shows that:

i) for a 1st melting (1st PAS), ΔH_M shifts from 23.5 to 24.0 J/g for a poly *RS* and from 26.1 and 33.0 to 29.5 and 37.0 J/g for poly *S* and poly *R* respectively,

ii) with a chiral initiator (Table 2), ΔH value of T_g for a 2nd PAS is about four times higher than for a 1st PAS and only three times higher with an achiral initiator (Table 1), in both case for a poly *RS*.

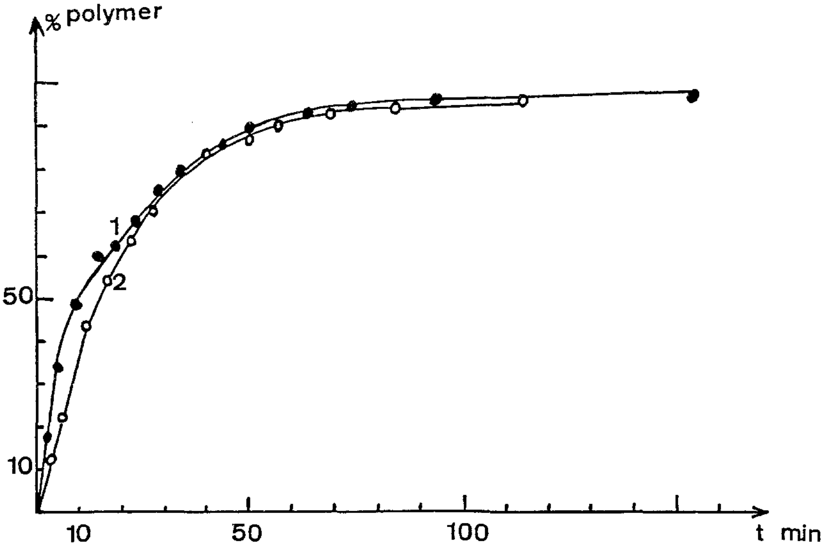

Fig. 1 3-benzyl-3-ethyl 2-oxetanone – Polymerization with NBu4 (S)-2-methylbutyrate curve 1: S-lactone, curve 2: R-lactone

Table 3 Variations of T_M and of ΔH_M of poly R and poly S melting after various thermal histories

		1st melting			2nd melting			3rd melting			4th melting		
						cycles 160°–200°C			cycles 160°–213°C			cycles 170°–223°C	
				(onset)			(onset)			(onset)			(onset)
S (nb)	T_M/°C	(0)	219	(192.6)	(6)	214.0	(203.8)	(10)	219.6	(216.1)		–	
	ΔH_M / J·g^{-1}		26.0			23.5			13.3			–	
R (nb)	T_M/°C	(0)	231.0	(207.5)	(6)	231.8	(213.3)	(7)	231.3	(215.0)	(6)	231.7	(225.3)
	ΔH_M / J·g^{-1}		33.0			31.6			31.6			24.3	

(nb): number of cycles

The fact that the melting temperatures T_M do not change indicates a poor stereoselection of the polymerization. Yet the fact that ΔH_M increases by 13% (poly *S*) and by 12% (poly *R*) involves that some stereoselection occurs during the polymerization, mainly during the initiation. The higher the *ee* is, the better the stereoselection should be. In our kinetic study, however, the highest rate of polymerization has been obtained when initiator and monomer had the same (S) configuration [7], which is not the case of R monomer and (S)-2-methylbutyrate (Fig. 1). In Fig. 1, the difference between R and S curves until about 30 min should be higher but the *ee* of S monomer is lower than that of the R one. In addition after 30 min the true initiator, i.e. terminal COO^-, is R or S configuration with mainly R or S monomer present, which gives the same propagation rate. (Fig. 1).

We have used a technique consisting of heating-cooling cycles [9, 10] for poly R and poly S to give them a well defined thermal history.

These results show that:

i) onset values T_m vary from 192 to 216°C for poly *S* and from 207 to 225°C for poly *R*, whereas the higher melting peak T_M does not shift,

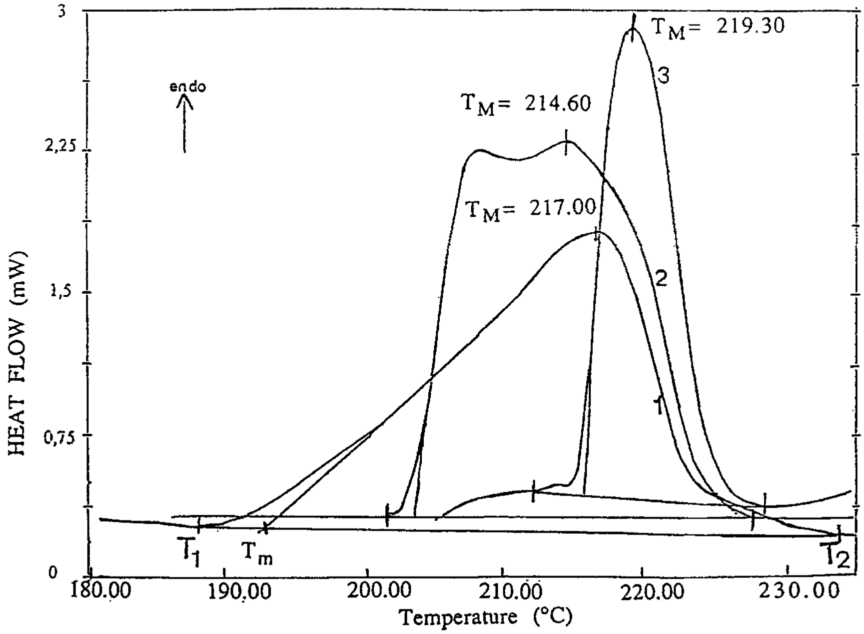

Fig. 2 Melting of S polymer with various thermal history (heating-cooling cycles) curve 1: first melting, curve 2: 6 cycles, 2 cycles 150°–190°C, 2 cycles 160°–200°C, 2 cycles 165°–205°C, curve 3: 10 cycles 160°–210°C

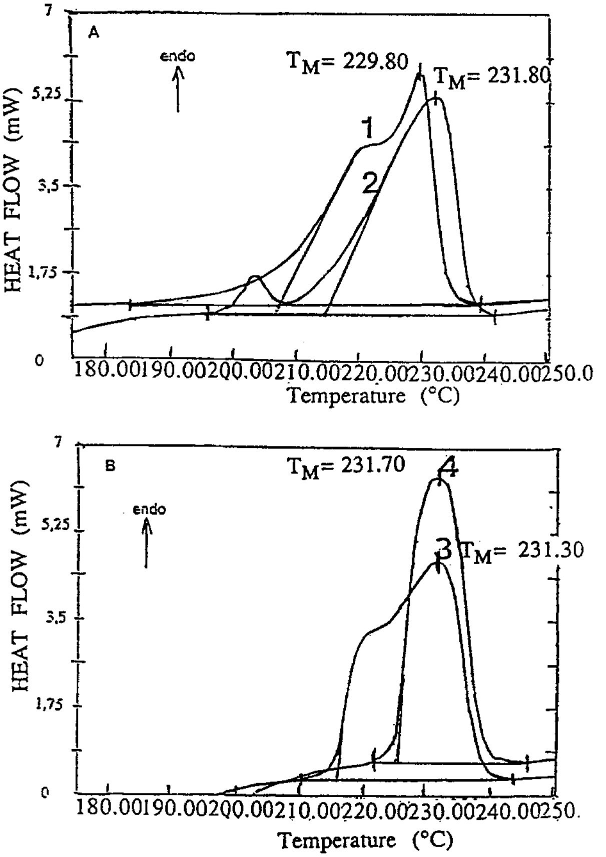

Fig. 3 Melting of R polymer with various thermal history (heating-cooling cycles) curve 1: first melting (no thermal history), curve 2: 6 cycles 150–190°C, curve 3: 7 cycles, 4 cycles 150–200°C, 3 cycles 175–213°C, curve 4: 6 cycles 170–223°C

ii) there are two melting peaks except when the temperature maximum of the cycles is higher than that of the 1st peak, in that case only one melting peak is observed (Figs 2 and 3),

iii) the lower the *ee* is, the higher the decrease of ΔH_M of melting (about 10% then 50% for poly *S* and 4% then 26% for poly *R*). In addition, the values of ΔH_M of the high melting form are lower than the values of two forms together (50 and 26%). The decrease of ΔH_M values may be due to two reasons: a) the ΔH_M of the high melting form may be lower than ΔH_M of the 'raw' sample (1st melting), b) a racemization may occur when the sample is melted above 210°C, poly *S* twice and poly *R* three times are melted above this temperature, before the high melting form is obtained. Above 210°C the transesterification begins to be effective. Then a rather low cooling rate of the melted polymer from about 270°C (end of melting peak) let the sample stay a rather long time in a liquid state at temperature above 210°C. Since in the poly *S* the proportion of R is higher than the proportion of S in a poly *R*, a higher shift of ΔH_M values, 50% instead of 26%, is obtained.

Table 4 Glass transition (T_g), crystallization and melting (T_M and ΔH_M of a polyracemate (50–50 mixture of poly *R* and of poly *S*)

	T_g /		Crystallization /		Melting /	
	°C	J/g·deg	°C	J/g	°C	J/g
1st PAS	68.0	0.56	117.0/127.0	–11.8	192.0/212.0	19.2
2nd PAS	65.6	0.30	141.3/153.0	–18.2	194.2/213.6	18.2
3h at 250°C	68.5	0.20	146.0/168.0	–14.8	195.0/215.0	13.9
5h at 250°C	70.8	0.23	153.0/168.9	–13.4	194.5/215.0	14.1
20h at 250°C	71.5	0.14	– –	–	200.0/215.0	0.79

1st PAS: first melting, 2nd PAS: second melting after slow cooling (rate 20 deg/min), heating rate: 20 deg/min, the polymer was kept melted 3, 5 and 20h at 250°C

We have also prepared a polyracemate (separate from poly *RS*), a mixture 50–50 wt. of poly *R* and poly *S*.

These results show that:

i) for the 1st PAS, there is a 'cold' crystallization after the glass transition at about 120°C (maximum of the peak), this maximum shifts to about 150°C (for 2nd PAS and higher) and disappears when the polymer has been kept 20 h at 250°C,

ii) the maximum of the melting peak is situated at 215°C, that is 68°C above the poly *RS* value (poly *R*: 84°C, poly *S*: 72°C). The shifts of ΔH_M values are higher: ΔH_M polyracemate: 19.2 J/g, poly *S*: 26.1 and poly *R*: 33.0 J/g,

iii) some racemization occurs from 1st PAS ($\Delta H_M = 19.2$ J/g) to 2nd PAS ($\Delta H_M = 18.2$ J/g) and mainly after 3 and 5 h of melting at about 250°C ($\Delta H_M = 14$ J/g). The polymer is melted some minutes between 215° and 270°C (2nd PAS) and in addition is kept 3 or 5 h at 250°C, temperature at which the transesterification is very effective, which may explain the racemization. The shift of the energy liberated during the crystallization from –18 J/g to –14.8 and –13.4 J/g is in favour for the above explanation,

iv) then the polyracemate, heated 20 h at 250°C, is converted into a poly *RS* type polymer. The peak remaining at 215°C is very weak, but the conversion polyracemate-poly *RS* is not complete even after 20 h. Anyway, ΔH_M

decreases from 19.2 to 0.79 J/g, i.e. 96% of racemization. No melting at 147°C can be observed, since a melted poly *RS* does not crystallize on cooling. The values observed for T_g (71°C and 0.14 J/gdeg) does not correspond to that of Table 1 (65° and 70°C, 0.28 and 0.85 J/gdeg for poly *RS*) because the statistical racemization of a polyracemate does not lead to a same poly *RS* type as a poly *RS* obtained by direct polymerization of a RS monomer.

The results of 1st PAS are very different from those obtained by Prud'homme *et al.* [10]. According to these authors, the racemate of 3-ethyl-3-propyl 2-oxetanone melts about 40°C is higher than pure poly *R*/poly *S*. They have also shown by X-ray diffraction that the polyracemate has its own structure. In the case of 3-ethyl-3-phenyl 2-azetidinone, there is a little difference for T_M values (about 4°C) between poly *R*/poly *S* and polyracemate [11], for the latter the X-ray diffraction has shown its own structure.

References

1 F. J. Carrière and C. D. Eisenbach, Macromol. Chem., 182 (1981) 325.
2 F. J. Carrière, R. Blottiau and H. Sekiguchi, Eur. Polym. J., 22 (1986) 285.
3 F. J. Carrière, R. Blottiau and H. Sekiguchi, Macromol. Chem., 189 (1988) 717.
4 J. Cornibert, R. H. Marchessault, A. E. Allegrezza and R. W. Lenz, Macromolecules, 6 (1973) 676.
5 T. Biela, S. Penczek, S. Slomkowski and O. Vogl, Macromol. Chem., 184 (1983) 811.
6 J. Cornibert and R. H. Marchessault, Macromolecules, 8 (1975) 296.
7 F. J. Carrière and R. Blottiau, Bull. Soc. Chim., (France) (in press).
8 F. J. Carrière and H. Sekiguchi, C. R. Acad. Sci. Ser. C, 281 (1975) 511.
9 F. J. Carrière and H. Sekiguchi, Chem. Zvesti, 30 (1976) 281.
10 D. Grenier and R. E. Prud'homme, J. Polym. Sci. Phys. Chem. Ed., 21 (1984) 577.
11 C. Bui, Thèse, Université Pierre et Marie Curie, Novembre 1990.

Zusammenfassung — Die Polymerisation von 3-benzyl-3-ethyl 2-oxetanon führt zu drei Polymer Typen: Poly *RS* (Überschuss des Enantiomers, $EE = 0$), Poly *R* oder Poly *S* (REE > SEE) und Polyracemate. Alle Polymere sind kristallin und die thermischen Eigenschaften (T_g, Schmelze T_M und ΔH_M) hängen wesentlich von *EE* des Polymers ab. Die Fortpflanzung der Polymerisation ist nicht stereospecifisch. Die Verwendung von Aufheitzen Abkühl Zyklen führt zu einer reinen kristallinen Form, die bei der höchsten Temperatur schmilzt. Das Polyracemat verhält sich wie ein reines Polymer, das bei niedrigeren Temperatur schmilzt; es racemisiert im Laufe einer verlängerten Erhitzung im Schemlzfluss.