N.m.r. spectroscopy of polyesters from bridged bicyclic lactones

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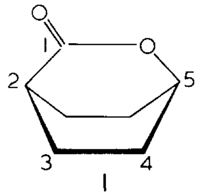
The ^{13}C n.m.r. spectra of some polyesters produced by anionic ring-opening polymerization of 2-oxabicyclo[2,2,2] octan-3-one are reported and discussed. From a comparison with the spectrum of the monomer and by hydrolysis of the polymer, it was possible to assign to the polymer, obtained using n-butyllithium as a catalyst, a microstructure in which the ester groups on the 1 and 4 positions of the cyclohexane unit are *cis* to each other. The polymers obtained both by sodium tert-butoxide and sodium–potassium alloy as initiators, showed spectral differences associated with the presence of another isomeric structural unit. Decreasing of the relaxation times (T_1) of *cis* unit by increasing the concentration of this new unit was reasonably explained by assuming for this latter a *trans* structure linked with the *cis* unit to form a stereocopolymer.

INTRODUCTION

This research on the ring-opening polymerization of 1,4-bridged cyclohexane lactones, stimulated by previous n.m.r. studies on the polymerization of oxyheterocycles[1,2], was undertaken with the aim of developing easy routes for the polymerization of oxygen-containing monomers and to explore the possibility, starting from the same monomer, of preparing polyesters of differing stereochemistry.

The present work deals with the structural characterization by n.m.r. spectroscopy of some low- and high-molecular-weight polyesters obtained from 2-oxabicyclo[2,2,2] octan-3-one (**1**) with different anionic initiators.



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EXPERIMENTAL

Spectra

^{13}C N.m.r. spectra were measured with a Bruker WH90 spectrometer operating at 22.63 MHz. Data were collected on 16 K memory and Fourier transformed. A pulse of 20° was applied with proton broad band decoupling and a sweep width of 100 Hz/cm. Relaxation times were measured using a $5T_1$, 180°, τ, 90° sequence, automatically controlled and computer programmed. ^{13}C spectra were carried out in $CDCl_3$ + TMS solution. ^{13}C chemical shifts are in ppm from internal TMS.

Materials

2-Oxabicyclo [2,2,2] octan-3-one (**1**) was synthesized according to the procedure of Giudici *et al.*[10]. The crude crystalline lactone obtained by vacuum distillation of the reaction mixture was purified by crystallization several times from ethylether and vacuum sublimed (m.p. 127°C).

Solvent. Toluene was purified as described by Weissberger[11]. Toluene was fractionated over sodium and then collected under nitrogen into a reservoir containing calcium hydride attached to the vacuum line. Finally the solvent was carefully degassed.

n-Butyllithium. The commercial Fluka product in n-hexane solution was used as received.

Sodium tert-butoxide was prepared under nitrogen by reaction of tert-butyl alcohol with sodium. Excess of alcohol was removed under vacuum and the alcoholate was purified by sublimation.

Sodium–potassium alloy was used in the form of a mirror to present a large surface area to the monomer.

Polymerization procedure. All the polymerizations were carried out in glass apparatus sealed under high vacuum. The lactone monomer was introduced into the vacuum system by sublimation and then the required amount of distilled toluene was added. The solution was transferred *via* a break-seal into the reaction vessel containing the initiator and then allowed to stand in a thermostat. Insoluble polymer was recovered by adding an excess of methanol to the reaction mixture and then purified by reprecipitation using a solvent-precipitant combination of $CHCl_3$–CH_3OH acidified with HCl. Soluble polymers were recovered directly by precipitating the reaction mixture into CH_3OH.

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Table 1 Preparation conditions of various polymers of 2-oxabicyclo[2,2,2] octan-3-one (**1**)

Sample	Initiator (mol %)	Toluene (ml/g of monomer)	Temperature (°C)	Time hours	Yield (%)	$[\eta]^a$ (dl/g)	$\bar{M}_n$
A	n-BuLi (0.8)	4	25	6	95	–	5040^d
B	tert-BuONa (1.5)	6.4	25	7	82	–	4500^d
C^b						5.4	–
D^b	NaK alloy (5)	9.7	60	72	56^c	0.8	–
E^b						0.4	–

[a] Measured in $CHCl_3$ at 25°C

[b] C, D, E are fractions of the same polymer. C is a methanol-insoluble fraction (92% of the original crude polymer). Fractions Dand E were obtained by evaporating the mother liquor resulting from the precipitation of polymer by pouring a $CHCl_3$ solution into methanol

[c] Total yield

[d] Measured by vapour phase osmometry (VPO)

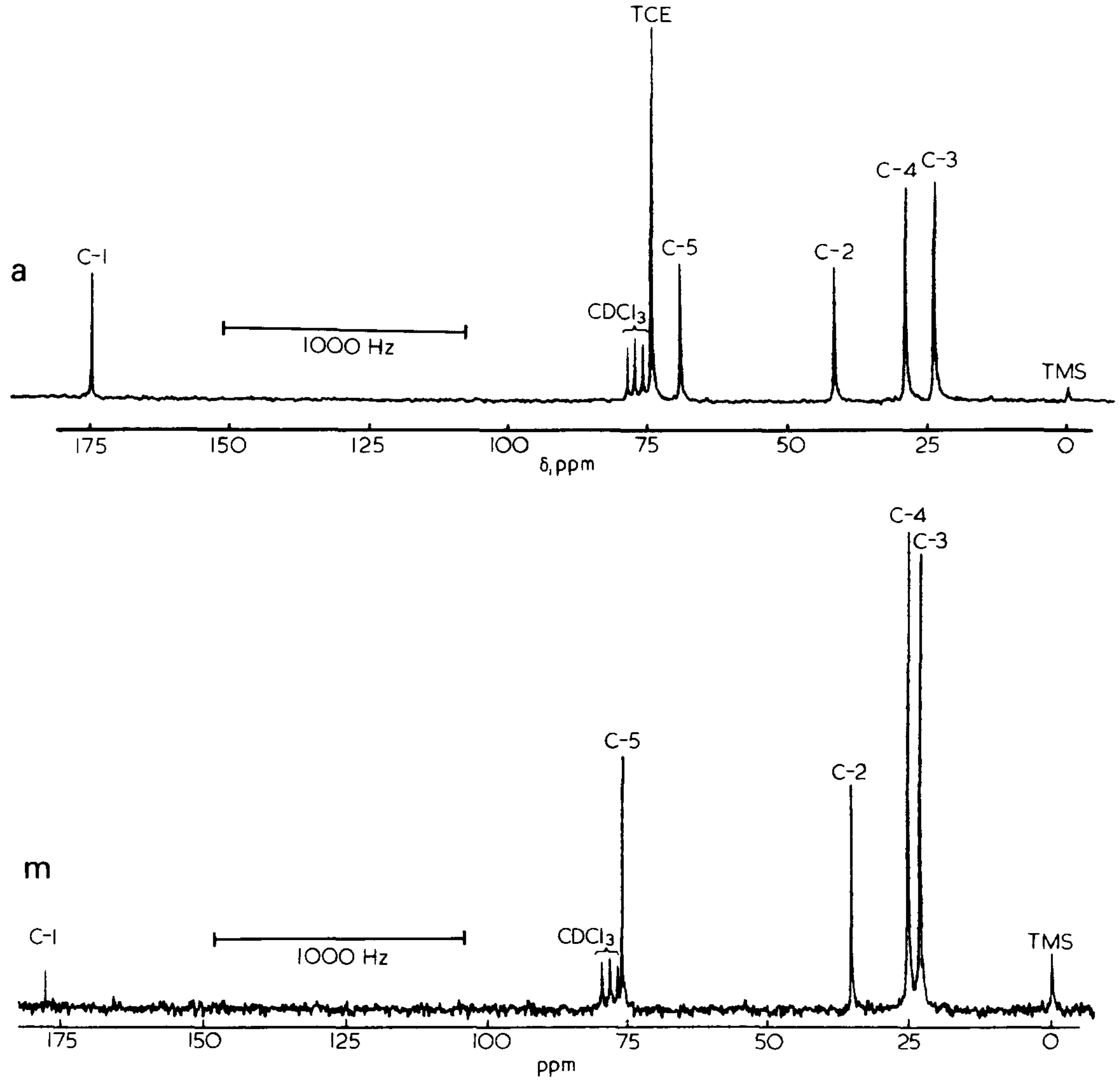


Figure 1 ^{13}C n.m.r. proton noise decoupled spectra (22.6 MHz) of 2-oxabicyclo[2,2,2] octan-3-one (m) and polymer sample A (a): (m) 100 mg/ml in $CDCl_3$ at 35°C; (a) 80 mg/ml in $CDCl_3$ 80%/1,1,2,2-tetrachloroethane (TCE) 20% at 35°C

Hydrolysis of polyester A. A mixture of 200 ml 0.1 N NaOH aqueous solution, 30 ml of dioxane and 3 g of polyester was refluxed for five days under a nitrogen atmosphere. Dioxane was added to facilitate the contact of the alkaline solution with the polymer which hydrolyses only with difficulty. The solution was then filtered and neutralized. After extraction with ethylether 0.08 g of a crystalline hydrolysis product melting at 152°C were recovered.

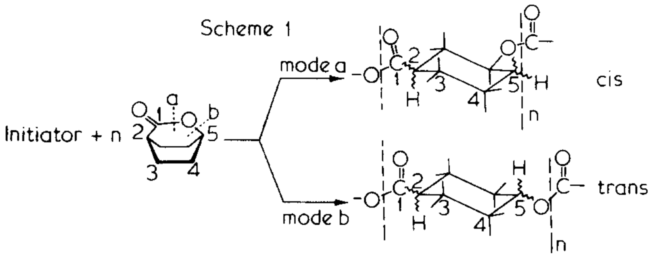
Cis-4-hydroxycyclohexane-1-carboxylic acid was synthesized from 2-oxabicyclo[2,2,2] octan-3-one according to the procedure described by Campbell *et al.*[12].

RESULTS AND DISCUSSION

In this study five polymer samples were examined, the polymerization conditions of which are listed in *Table 1*.

It is well recognized that anionic polymerization of lactones can proceed by two modes. The first (a) involves the acyl-oxygen cleavage of the ring and the propagating species are alkoxide groups, while the second (b) (S_N2 mechanism) arises from alkyl-oxygen cleavage of the ring, and the active species are carboxylate groups[3,4]. Assuming both of these mechanisms to be operative for the polymerization of **1**, it follows that two polymers with different configuration of the structural unit (i.e in which the two ester groups on the cyclohexane ring are *cis* and *trans* to each other) may be produced, as shown in Scheme 1.

Scheme 1



The ^{13}C n.m.r. spectra of solution of the lactone monomer (**1**) and of the corresponding polymer A obtained with n-BuLi as the initiator, are reported in *Figure 1*.

Since no ^{13}C n.m.r. spectra have yet been reported for these compounds, the assignment of signals of (**1**) was made by comparison with the limited chemical shift data of available related monocyclic lactones[5]. The assignment of the carbonyl and methine carbons were easily confirmed by their singlet or doublet splitting observed in off-resonance decoupled spectra. The signals due to the methylene carbons between 23 and 26 ppm could not be unambiguously assigned to C–3 and C–4 with the same decoupling technique. Selective decoupling, generally very effective for this kind of assignment, was unsuccessful because of the overlapping of the H_3 and H_4 signals even at very high magnetic fields (63.42 kgauss). Thus, taking into account the deshielding effect of the ester oxygen, the peak at 25.31 ppm should correspond to the methylene carbon C–4 closer to the heteroatom.

Table 2 ^{13}C n.m.r. chemical shifts at 22.6 MHz of the lactone monomer (**1**) and of the polymer obtained with n-BuLi in toluene at 25°C. (Negative sign means upfield shift.) $CDCl_3$ solutions. TMS internal reference

Carbons	$\delta_{monomer}$(ppm)	$\delta_{polymer}$(ppm)	$\Delta\delta$ (polym. -mon)
C–1	177.17	174.61	−2.56
C–2	35.18	41.59	+6.41
C–3	23.24	23.92	+0.68
C–4	25.31	29.00	+3.69
C–5	75.28	69.07	−6.21

The ^{13}C n.m.r. spectrum of polymer A exhibits five distinct resonances, the chemical shifts of which differ slightly from those found for the lactone monomer. Infra-red analysis confirmed the absorptions of C=O and C–O stretching at 1735 and 1163 cm^{-1}, respectively. The number of these signals and the i.r. data are in agreement with a breaking of the ester bond of the monomer. The rather small upfield shift of the carbons C–1 and C–5 and the low deshielding of carbons C–2, C–3 and C–4 (see *Table 2*) provide insufficient evidence of unambiguously assign the structural unit of the polymer. For this reason the polymer A was hydrolysed and the ^{13}C n.m.r. spectrum of the crystalline hydrolysis product was examined. This spectrum was identical with that of an authentic sample of *cis*-4-hydroxycyclohexane-1-carboxylic acid *(Figure 2)*. Since it is known that acyclic esters hydrolysed by acyl-oxygen fission[6,7] the above observation definitely established that the polymer A was a polyester of lactone **1** having the *cis* cyclohexane structural unit (Scheme 1). From a stereochemical viewpoint this result demonstrates that the polymerization of **1**, initiated by n-BuLi, propagates only through an acyl-oxygen ring-opening mechanism and this is in agreement with the strong nucleophilic character of the initiator used[3,4]. This conclusion is supported by the high resolution ^{1}H n.m.r. spectrum which clearly showed the methyl resonance of the n-butyl group incorporated into the polymer.

In *Figure 3* are reported the ^{13}C n.m.r. spectra of the polymer samples B and C obtained with tert-BuONa and NaK alloy, respectively. These spectra are more complex than those of the polyester A. Indeed, they show eight resonances of non-carbonyl carbon atoms, four of which are coincident with those of the homopolymer A. This pattern suggests the presence of another structural unit (starred carbons) which may be an isomer of the previously assigned

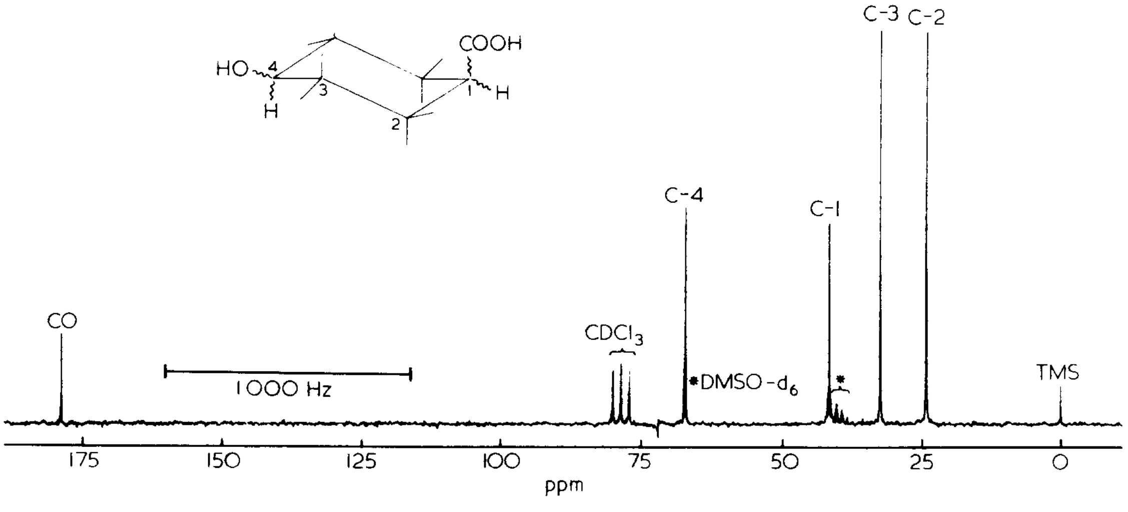


Figure 2 ^{13}C n.m.r. proton noise decoupled spectrum (22.6 MHz) of a reference sample of *cis*-4-hydroxycyclohexane-1-carboxylic acid. 100 mg/ml in $CDCl_3$/DMSO-d_6 (85%/15% v/v). Chemical shifts: CO, 177.6; C-4, 66.38; C-1, 41.00; C-3, 32.0; C-2, 23.73

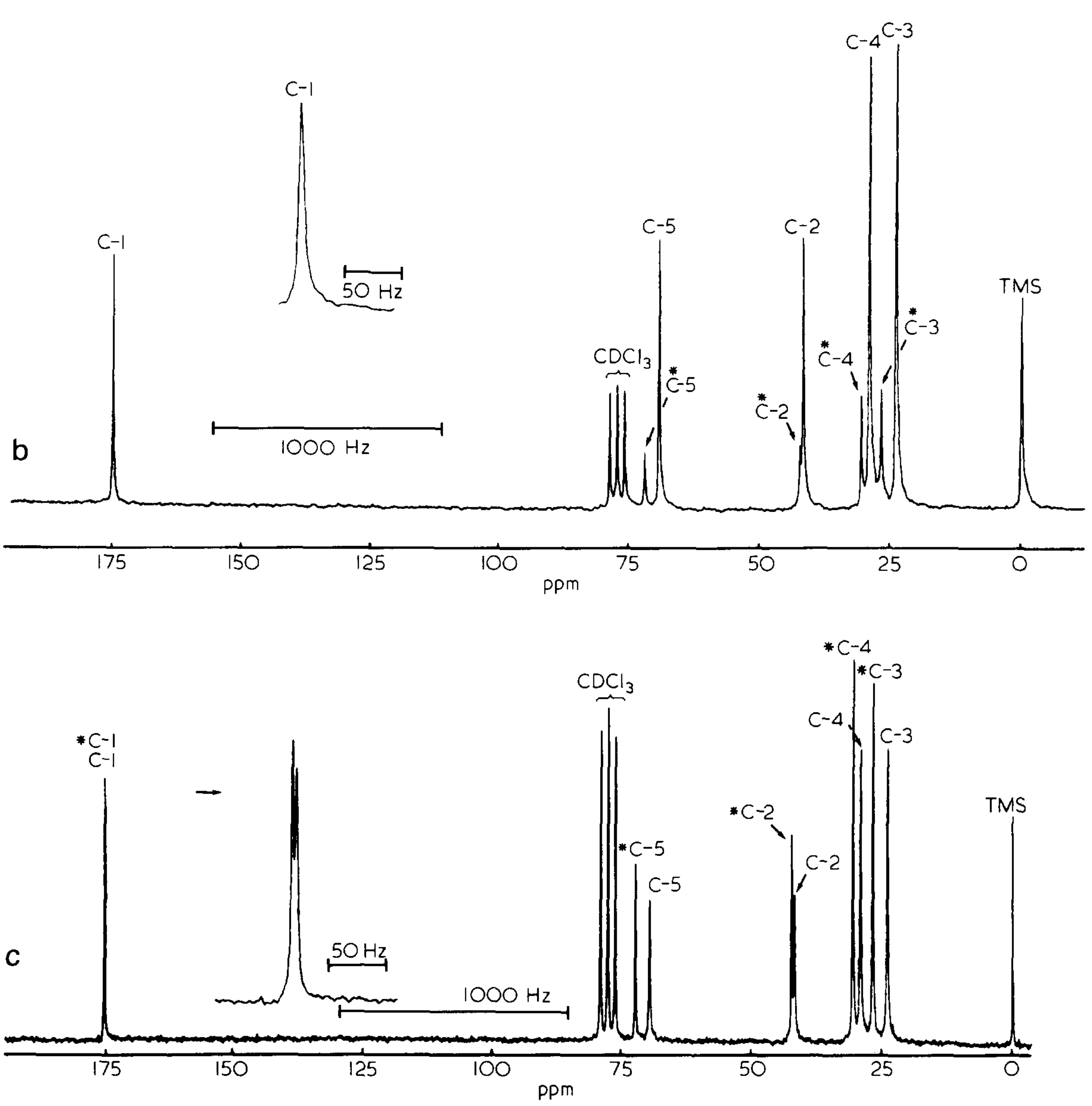


Figure 3 ^{13}C n.m.r. proton noise decoupled spectra (22.6 MH_z) of the polymer samples B(b) and C(c): (b) 100 mg/ml in $CDCl_3$ at 35°C; (c) 40 mg/ml in $CDCl_3$ at 35°C

cis unit. This suggestion is confirmed by the splitting of the carbonyl resonance which is clearly evident in the spectrum *c*, while it appears unresolved in the spectrum *b*. This is certainly due to the low relative concentration of the presumed isomeric form in sample B. The spectrum does not show marked change on going from the sample C, of very high molecular weight, to the samples D and E, of lower molecular weight.

In *Table 3* the ^{13}C chemical shifts and the ratios between the *cis* structural unit (α) and the presumed isomer (β) for the polymers A, B, C, D and E are reported.

The relaxation mechanism is not purely dipolar, probably due to contribution from intramolecular motion of the cyclohexane ring. Increasing the concentration of the new β structural unit reduces the relaxation times of the carbons in the α form as a consequence of the reduced mobility of these carbons.

Different mobilities of the two α and β units can be explained on the basis of the conformational equilibrium bet-

Table 3 ^{13}C n.m.r. chemical shifts (at 22.6 MHz) for the carbons of the *cis* structural unit (α) and of its presumed geometrical isomer (β) and β/α ratios in the various polymers. $CDCl_3$ solutions. TMS internal reference

Carbon		Polymer				
		A	B	C	D	E
C–1	β	–	174.53	174.70	174.62	174.76
	α	174.44	174.14	174.55	174.45	174.50
C–2	β	–	42.16	42.21	42.29	42.21
	α	41.39	41.63	41.69	41.63	41.62
C–3	β	–	26.74	26.77	26.73	26.77
	α	23.73	23.90	23.98	23.99	23.98
C–4	β	–	30.49	30.58	30.50	30.55
	α	28.80	28.98	29.07	29.42	29.07
C–5	β	–	71.85	71.85	71.82	71.85
	α	68.87	69.10	69.26	69.33	69.17
$\frac{\beta}{\alpha}$	Ratio	$\frac{0}{100}$	$\frac{22}{78}$	$\frac{53}{47}$	$\frac{61}{39}$	$\frac{63}{37}$

The spin-lattice relaxation times (T_1) of the carbon atoms of the two units α and β for the polymers A, B, C, D and E are given in *Table 4*

Table 4 ^{13}C Spin-lattice relaxation times T_1 (msec) for carbon atoms of α and β units of the polymer samples A, B, C, D, E in $CDCl_3$ solution

		Polymer				
	Carbon	A	B	C	D	E
α	C–2	340	300	215	230	220
	C–3	190	200	135	115	135
	C–4	185	200	140	120	135
	C–5	320	290	240	160	220
β	C–2	–	340	385	410	350
	C–3	–	260	240	230	220
	C–4	–	230	235	240	225
	C–5	–	320	370	390	315

ween the relative conformers. In fact the *cis* configuration allows an axial–equatorial ⇄ equatorial–axial equilibrium for the substituents in the 2 and 5 positions.

On the other hand, the *trans* configuration can flip between diequatorial and diaxial conformations, the latter of which is severely sterically hindered. From this point of view, the decrease in the relaxation time T_1 of the carbons in the α form, caused by the insertion in the polymer chain of β units, allows us to assign to this unit the *trans* configuration. These results indicate that the α and β units are linked together to form a stereocopolymer chain, and that a mixture of α and β homopolymers can be excluded. The copolymer character is also indicated by the change observed in such properties as crystallinity, thermal stability and solubility. For instance, the low-molecular-weight homopolyester A is completely insoluble in toluene while the high copolyester C is soluble in the same solvent.

Comparison of relaxation times in samples C, D and E reveals a greater rigidity in sample D which has the intermediate molecular weight. Despite the different molecular weights, fractions C and E exhibit very similar spin-lattice relaxation times. This effect could be explained by different distributions of the *cis* and *trans* units in the three fractions.

A dependence of the dynamic n.m.r. parameters[8] on the molecular weight can be excluded and a correlation of these parameters with tacticity[9], as a consequence of the greater rigidity caused by the introduction of the *trans* units in a *cis* polymer, seems reasonable. This observation suggests that the polymer D probably has shorter alternating blocks than the C and E fractions.

In order to confirm that the major contribution to the spin–lattice relaxation time is due to the comformational transition between the axial–equatorial ⇄ equatorial–axial conformation for the *cis* configuration and between the diaxial and diequatorial for the *trans*, a low temperature ^{13}C n.m.r. study was carried out.

The ^{13}C n.m.r. spectrum at –40°C of the polymer sample E is reported in *Figure 4*. From a comparison with the corresponding spectrum at room temperature, it is possible to observe a small splitting of C–5, C–2, C–4, C–3 resonances in the α form. The lack of any splitting for the β form could be due either to lower interconversion energy barrier or to different relative populations of the diaxial and diequatorial forms or to accidental chemical shift equivalence in both conformers.

In conclusion, the present ^{13}C n.m.r. study permits the detection and the determination of geometrical isomerism in polyesters prepared by anionic polymerization of 2-oxabicyclo [2,2,2] octan-3-one (**1**). The structural heterogeneity of the copolymers is due to the presence of cyclohexane units in which the ester groups on the position 1 and 4 are *cis* and *trans* to each other.

From a sterochemical viewpoint, the possibility of obtaining two geometrical isomers through only one ring-opening process of **1** can be taken into account only if the mode 'b' fission (Scheme 1) occurs by S_N1 mechanism. In particular, this mechanism might take place if the nucleophilic attack on the secondary carbon C_5 is so slowed that the normally slow alkyl-oxygen unimolecular cleavage of the ester bond, involving the carbenium ion, takes over.

Such a mechanism, which leads to the incorporation of both *cis* and *trans* units into the same polymer chain, seems however unlikely because it appears conceivable only for more substituted and strained lactones which are able to produce stable carbenium ions.

Obviously, if the alkyl-oxygen cleavage occurs by S_N2 mechanism, the inversion of configuration of C_5 leads to *trans* structure of the active 1,4-disubstituted cyclohexane carboxylate species.

When the initiator attacks the C=O at the carbon (mode 'a' fission), regardless of the mechanism, only the *cis* configuration of the propagating alkoxide ion is obtained, since the carbonyl is external to the cyclohexane ring.

Assuming that the alkoxide and the carboxylate propagating groups can change their sites of attack on the lactone monomer, the formation of *cis–trans* copolymer could be explained by the contribution of both acyl-oxygen and alkyl-oxygen fission to the propagation reaction. Of course, such a process would lead to structural irregularities at the joining points of the isomeric polymer units such as ether and anhydride linkages. The apparent lack of their spectroscopic evidence is probably due to long sequences of isomeric structural units producing insufficient concentration of such irregularities.

Moreover, the number of anhydride linkages can be further lowered as a consequence of their well-known low stability toward hydrolysis.

The highest molecular weight polymer C provides an interesting example of a new stereocopolymer which can be converted into tough, transparent and flexible films.

ACKNOWLEDGEMENT

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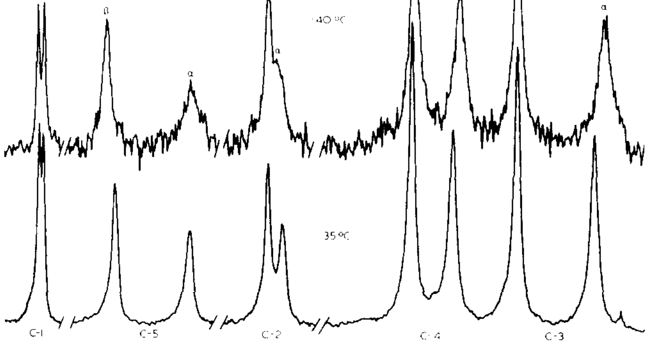

Figure 4 ^{13}C n.m.r. spectrum at –40° C of the polymer E

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