Study of bulk chain-coupling reactions

IV. Synthesis of poly(polyester-block-polyamide) using 2,2'-bis(2-oxazoline) or 2,2'-bis(5,6-dihydro(4 H)-1,3-oxazine) as chain-coupling agents

Abderrahim Douhi, Alain Fradet *

Laboratoire de Synthèse Macromoléculaire, CNRS, URA n° 24,
Université Pierre et Marie Curie, Case 184, 4, Place Jussieu, F-75252 Paris Cedex 05, France

Summary

Block copolymers containing polyester and polyamide blocks have been prepared by the bulk reaction of the corresponding carboxy-terminated polymers with 2,2'-bis(2-oxazoline) or 2,2'-bis(5,6-dihydro-(4H)-1,3-oxazine) as chain-coupling reagents (**CC**). A two-step reaction has been used, involving (i) the reaction of polyamide with **CC** excess, and (ii) the addition of polyester, leading to a random distribution of blocks in the final block-copolymer. ^{1}H and ^{13}C NMR studies show that the coupling reaction takes place in the expected way. The stability of the resulting polymers is higher than that of the starting oligomers, and DSC indicates a phase separation between polyester and polyamide phases.

Introduction

In previous articles (1,2) we have described the synthesis of block copolymers by the bulk reaction of mixtures of α,ω-diamino oligomers with bisoxazolones as chain-coupling reagents (**CC**). These **CC**'s give fast polyaddition reactions with amino end groups. The expected high molar mass block-copolymers were obtained more rapidly than using the classical bulk reaction between oligomers bearing mutually reactive end-groups. The potential application of the method is the reactive extrusion of oligomer(s)/**CC** mixtures at temperatures in the 180-250°C range, i.e. applicable to polymers such as polyamides.

Among the various reactions which can be applied to oligomer coupling, the reaction between carboxy-terminated oligomers and bisoxazolines or bisoxazines is particularly interesting. Bisoxazolines or bisoxazines have been used as chain extenders for poly(ethylene terephthalate) or poly(1,4-butylene terephthalate) by high temperature reaction in the bulk with residual carboxy groups (3-5). On the other hand, we have shown (6) that the reactions of carboxy terminated aliphatic polyamides and polyesters with bisoxazolines or bisoxazines are fast (80% conversion in 10 min reaction) and yield high molar mass polymers. This article presents our first results on the synthesis of block copolymers using this chemistry : α,ω-dicarboxy poly(2,2'-oxydiethylene succinate) (**PS**) ($\overline{M_n}$ ≈ 1000) and α,ω-dicarboxy polyamide 12 (**PA**) ($\overline{M_n}$ ≈ 1000) have been reacted with 2,2'-bis(2-oxazoline) (**C1**) or 2,2'-bis(5,6-dihydro-(4H)-1,3-oxazine) (**C2**) to give aliphatic poly(polyamide-block-polyester).
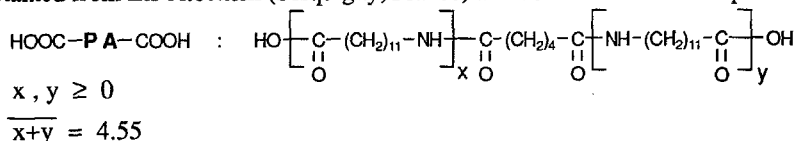
* Corresponding author

It must be pointed out that it is usually difficult to obtain poly(polyester-block-polyamide) by the classical bulk reaction between oligomers bearing mutually reactive end groups : due to very long reaction time, the extent of the ester/amide interchange reaction increases, resulting in materials with a marked random character.
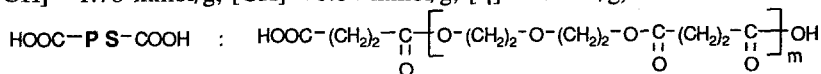
Experimental
Materials
Starting materials and solvents were commercially available (≥99% from Prolabo or Aldrich Co.) and were used without further purification. Carboxy terminated polyamide 12 (PA) ([COOH] = 1.915 mmol/g, chain limiter adipic acid, free adipic acid : 0.43 wt %) was obtained from Elf-Atochem (Serquigny, France) and used without further purification.

$$HOOC-\mathbf{P\,A}-COOH \quad : \quad HO\left[\!\!\begin{array}{c} C-(CH_2)_{11}-NH \\ \| \\ O \end{array}\!\!\right]_x \!\!\begin{array}{c} C-(CH_2)_4-C \\ \| \quad\quad \| \\ O \quad\quad O \end{array}\!\!\left[\!\!\begin{array}{c} NH-(CH_2)_{11}-C \\ \| \\ O \end{array}\!\!\right]_y\!\!OH$$

$x , y \geq 0$

$\overline{x+y} = 4.55$

The synthesis of α,ω-dicarboxy poly(2,2'-oxydiethylene succinate) (PS) ([COOH] = 1.78 mmol/g, [OH] < 0.01 mmol/g, [η] = 0.1 dL/g) is described in ref (6).

$$HOOC-\mathbf{P\,S}-COOH \quad : \quad HOOC-(CH_2)_2-\!\!\begin{array}{c} C \\ \| \\ O \end{array}\!\!\left[\!\!\begin{array}{c} O-(CH_2)_2-O-(CH_2)_2-O-\!\!\begin{array}{c}C\\\|\\O\end{array}\!\!-(CH_2)_2-\!\!\begin{array}{c}C\\\|\\O\end{array} \end{array}\!\!\right]_m\!\!OH$$

The syntheses of bisoxazoline C1 and bisoxazine C2 were carried out by alkaline dehydrohalogenation of bis(chloroalkyl) oxamides as previously described (6,7).

Reaction between dicarboxy oligomers and C1 or C2.
In a 50 mL reaction kettle equipped with a regulated oil bath, nitrogen inlet and outlet, and mechanical stirrer, 10.00 g (9,58 mmol) of PA and 2.684 g (19.17 mmol) of C1 were heated at 240°C for 10 min. 6.00 g of the resulting compound were heated to 200°C for 160 min with 5.10 g (4.54 mmol) of PS. Samples were withdrawn at intervals to follow reaction progress.
The same procedure was used for the system PA/C2/PS.

Infrared spectroscopy (IR) : Spectra were recorded on a Bruker IFS 45 spectrometer. Solids were analyzed in KBr pellets and liquids in KBr wall cells.

NMR spectroscopy : Spectra were recorded on a Bruker WM250 spectrometer. In order to assign the class of carbon atom, DEPT and QUATD selective pulse sequences were used. Assignments were done using selective homo- and heteronuclear irradiations. The spectra of model compounds and of polyesters were recorded in CDCl$_3$ or in DMSO-d6. The spectra of polyamides and block copolymers were recorded in trifluoroacetic anhydride /chloroform-d (TFA/CDCl$_3$ 1/4 v/v) or 1,1,1,3,3,3-hexafluoro-2-propanol-d2/chloroform-d (HFIP/CDCl$_3$ 2/3 v/v) solutions. For comparison purposes, some of the spectra of model compounds were also recorded in TFA/CDCl$_3$ or HFIP/CDCl$_3$.
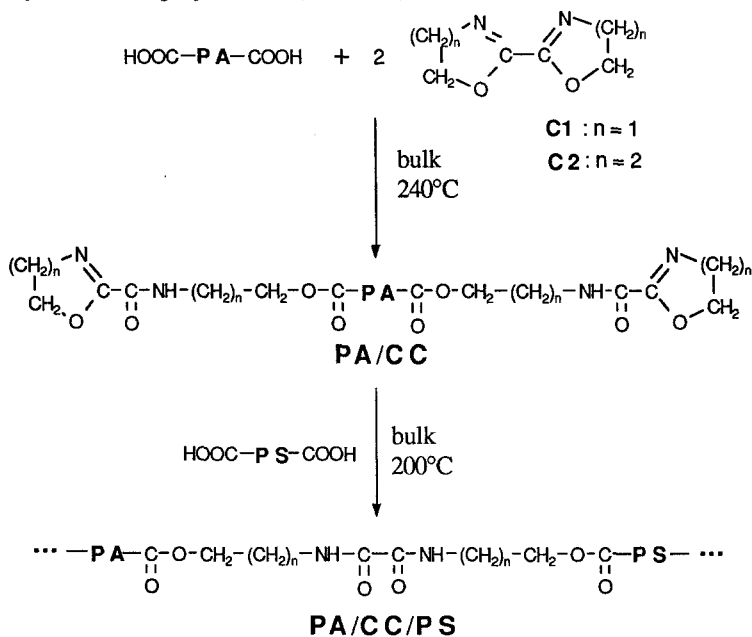
DSC and TGA were carried out on a DuPont Instruments 9900 apparatus equipped with DSC910 and TGA951 modules at a heating rate of 20°C/min (DSC) or 10°C/min (TGA).

The titration of carboxy groups was carried out using a Mettler DL40RC automatic titrator with 0.06 N KOH/ethanol solution. Samples were dissolved in benzyl alcohol.

Results and discussion
Preliminary experiments were carried out using the direct reaction of a mixture of the two oligomers and C1 or C2 at 200°C (one-step reaction). The results were not satisfactory. As previously shown, the reaction of C1 or C2 and PA requires temperatures in the range 220-250°C (6). However, to avoid any degradation of poly(2,2'-oxydiethylene succinate), the reactions involving this compound must be carried out at T ≤ 200°C.

Therefore, the following two-step procedure was used : In a first step, 1 mol **PA** was reacted with 2 mol **CC** at 240°C for 10 min, leading to an oxazoline- or oxazine-terminated polyamide (**PA/CC**). In a second step this intermediate was reacted at 200°C with 1 mol of the carboxy-terminated polyester **PS** (scheme 1).

$$HOOC-P\,A-COOH \quad + \quad 2$$

C1 : n ≈ 1
C2 : n ≈ 2

bulk
240°C

PA/CC

$$HOOC-P\,S-COOH$$

bulk
200°C

$$\cdots -P\,A-\overset{O}{\underset{\parallel}{C}}-O-CH_2-(CH_2)_n-NH-\overset{O}{\underset{\parallel}{C}}-\overset{O}{\underset{\parallel}{C}}-NH-(CH_2)_n-CH_2-O-\overset{O}{\underset{\parallel}{C}}-P\,S- \cdots$$

PA/CC/PS

Scheme 1

Sequence length distribution

The oxazoline-terminated polyamide **PA/CC** of scheme 1 represents the "number-average molecule" present in the medium at the end of the first step. Assuming equireactivity of functional groups, it is clear that a Flory-type distribution is actually obtained, with unreacted **CC** and CC-terminated polyamide chains of various DP : : **CC-PA-CC** (trimer), **CC-PA-CC-PA-CC** (pentamer), **CC-(PA-CC-)$_{(i-3)/2}$-PA-CC** ("i-mer").

At total conversion, the mol fraction of i-mers, $\overline{DP_n}$ and $\overline{DP_w}$ are given by Flory relations (9) :
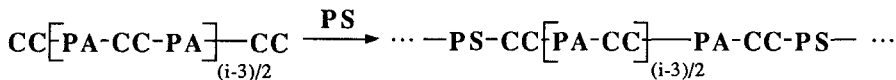
$$x_i = \frac{N_i}{\sum\limits_{i=1,3,5\,...} N_i} = (1-r)\,r^{(i-1)/2} \quad [1], \qquad \overline{DP_n} = \frac{1+r}{1-r} \quad [2], \qquad \overline{DP_w} = \frac{1+r+\dfrac{4r}{1+r}}{1-r} \quad [3]$$

where r is the ratio of **PA** to **CC** and N_i is the number of moles of i-mers. Here r=1/2, and leads to $\overline{DP_n}$ = 3, which is of course the DP of the "number-average" intermediate **PA/CC**.

The length of i-mers can be expressed using the number of PA blocks, j = (i-1)/2, instead of the number of **CC** and **PA** units, i. The mol fraction $x_{PA,j}$, defined as the number of molecules containing j **PA** blocks over the total number of **PA**-containing molecules, is :

$$x_{PA,j} = \frac{N_i}{\sum_{i=3,5,7\,...} N_i} = \frac{N_j}{\sum_{j=1,2,3\,...} N_j} = (1-r)\, r^{j-1} \qquad [4]$$

The distribution of **PA** blocks remains obviously unchanged after reaction with **PS** :

$$CC\left[PA\text{-}CC\text{-}PA\right]_{(i-3)/2}\!\!CC \xrightarrow{\ \ \textbf{PS}\ \ } \cdots -PS\text{-}CC\left[PA\text{-}CC\right]_{(i-3)/2}\!\!PA\text{-}CC\text{-}PS- \cdots$$

Consequently, relation [4] also gives the mol fraction of sequences composed of j **PA** blocks in the final block copolymer, that is the **PA** sequence length distribution of this copolymer. This distribution is a random one : For a copolymer containing r mol **PA** and 1-r mol **PS** randomly connected, the probability of the existence of a succession of j-1 **PA-PA** connections and one **PA-PS** connection is of course $(1-r)\, r^{j-1}$, identical to $x_{PA,j}$. At total conversion, a random distribution is obtained for the two-step reaction. The same distribution would be obtained if the reaction had been carried out in one step.

The number- and weight-average lengths of **PA** sequences in final block copolymer are (10,11) :

$$\overline{N_{n,PA}} = \sum_{j=1,2,3,...}(1-r)\, j\, r^{j-1} = \frac{1}{1-r} \quad [5] \qquad\qquad \overline{N_{w,PA}} = \sum_{j=1,2,3,...}(1-r)^2\, j^2\, r^{j-1} = \frac{1+r}{1-r} \quad [6]$$

In the present case r = 1/2, then : $\overline{N_{n,PA}}$ = 2 and $\overline{N_{w,PA}}$ = 3.

Study of reaction by ^{13}C NMR

In the spectrum of **PA/C1** there is no peak corresponding to the methylenes of oxazoline end groups. Two peaks appear instead, at 42.1 and 61.3 ppm, assigned to the methylenes of N-hydroxyethyl oxamide end groups ($-CO\text{-}CO\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}OH$). These groups result from the hydrolysis of oxazoline end groups by water present in the solvent used, a mixture of 1,1,1,3,3,3-hexafluoro-2-propanol-d2 (HFIP) and $CDCl_3$. This was confirmed using a model reaction between dodecanoic acid and **C1** in excess : The peaks due to oxazoline end groups are present in the spectrum recorded in $CDCl_3$ but are replaced in HFIP/$CDCl_3$ by the peaks corresponding to N-hydroxyethyl oxamide methylenes. The same phenomenon is observed on **PA/C2** solutions (Fig 1a).

The spectrum of **PA/C2** is given in fig. 1a. The presence of both adipamide (A) and dodecylamide (D) units in starting polyamide-12 is detected on some carbons. For instance, the amide carbonyls of polyamide chain give two resonances, labelled C^{1pA} and C^{1pD} at 176.8 and 175.9 ppm respectively. The resonances corresponding to the methylenes of the new $-COO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CO\text{-}CO-$ linkage appear at 62.4, 27.6 and 37.2 ppm. A/D peak splitting is observed for ester carbonyl C^{1pb} at 176.3 (A) and 177.2 (D) ppm, and for ester methylene C^{1bp} at 62.4 (D) and 62.6 (A) ppm. The new C^{3a} and C^{3b} CONH give two peaks close to 160 ppm. The same observations can be made from the **PA/C1** spectrum, in which, however, the C^{1pb} ester carbonyls are masked by the C^{1p} CONH carbonyls of polyamide chain. Some weak resonances arising from residual COOH groups can be seen close to 180 ppm for both **PA/C2** and **/C1**. Small peaks close to 157 ppm for **PA/C1** have been assigned to unidentified side reactions. Except for these weak peaks, all the expected resonances for an oxazoline or oxazine terminated polyamide are found.
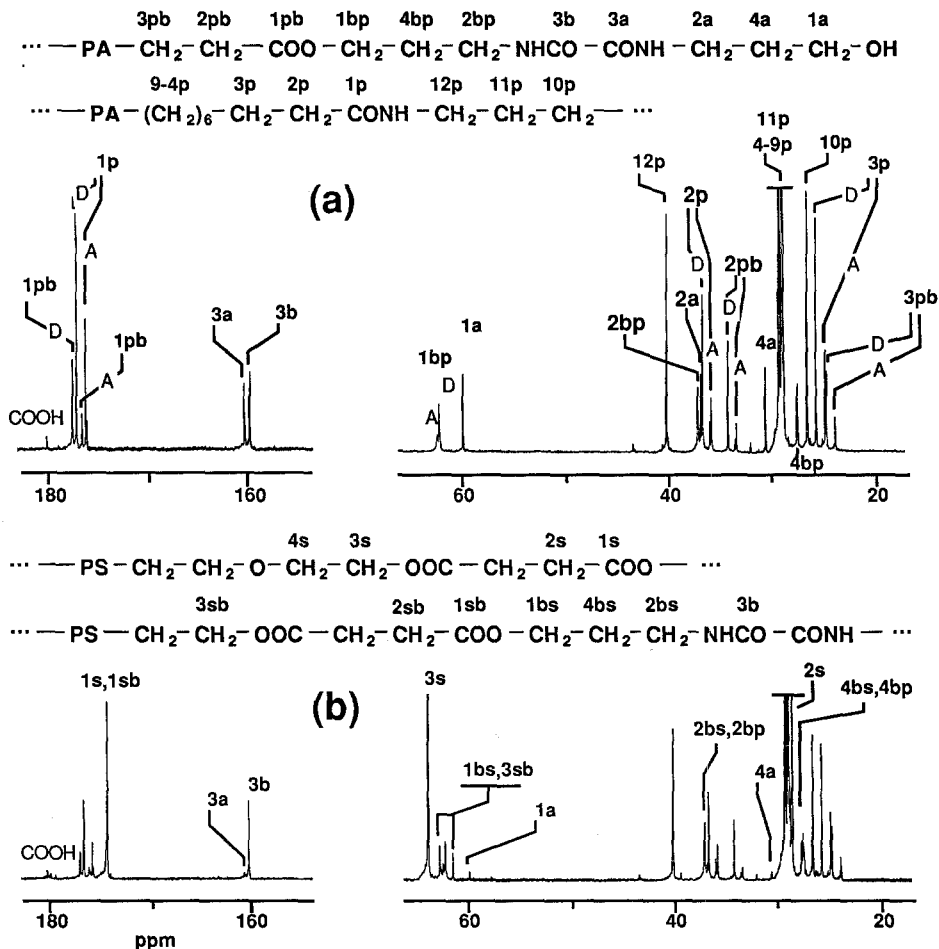
$$\cdots -\!\!-\,\overset{\text{3pb}}{\text{PA}}-\overset{\text{2pb}}{\text{CH}_2}-\overset{\text{1pb}}{\text{CH}_2}-\overset{}{\text{COO}}-\overset{\text{1bp}}{\text{CH}_2}-\overset{\text{4bp}}{\text{CH}_2}-\overset{\text{2bp}}{\text{CH}_2}-\overset{\text{3b}}{\text{NHCO}}-\overset{\text{3a}}{\text{CONH}}-\overset{\text{2a}}{\text{CH}_2}-\overset{\text{4a}}{\text{CH}_2}-\overset{\text{1a}}{\text{CH}_2}-\text{OH}$$

$$\cdots -\!\!-\,\overset{\text{9-4p}}{\text{PA}}-\overset{}{(\text{CH}_2)_6}-\overset{\text{3p}}{\text{CH}_2}-\overset{\text{2p}}{\text{CH}_2}-\overset{\text{1p}}{\text{CONH}}-\overset{\text{12p}}{\text{CH}_2}-\overset{\text{11p}}{\text{CH}_2}-\overset{\text{10p}}{\text{CH}_2}-\cdots$$

$$\cdots -\!\!-\,\overset{}{\text{PS}}-\overset{\text{4s}}{\text{CH}_2}-\overset{\text{3s}}{\text{CH}_2}-\overset{}{\text{O}}-\overset{}{\text{CH}_2}-\overset{}{\text{CH}_2}-\overset{}{\text{OOC}}-\overset{\text{2s}}{\text{CH}_2}-\overset{\text{1s}}{\text{CH}_2}-\overset{}{\text{COO}}-\cdots$$

$$\cdots -\!\!-\,\overset{\text{3sb}}{\text{PS}}-\overset{}{\text{CH}_2}-\overset{}{\text{CH}_2}-\overset{}{\text{OOC}}-\overset{\text{2sb}}{\text{CH}_2}-\overset{\text{1sb}}{\text{CH}_2}-\overset{\text{1bs}}{\text{COO}}-\overset{\text{4bs}}{\text{CH}_2}-\overset{\text{2bs}}{\text{CH}_2}-\overset{\text{3b}}{\text{CH}_2}-\overset{}{\text{NHCO}}-\overset{}{\text{CONH}}-\cdots$$

Figure 1 : ^{13}C NMR spectra (62.9 MHz, HFIP/CDCl$_3$, ref. TMS) of (a) **PA/C2** and (b) **PA/C2/PS**. See text for A and D.

After reaction with dicarboxy poly(2,2'-oxydiethylene succinate) (**PS**), the intensity of the peaks corresponding to **C2** end groups (C^{1-4a}) and to the COOH end groups of **PS** strongly decrease (Fig. 1b). On the other hand, the spectrum exhibits two new resonances at 61.7 and 63.1 ppm assigned to CH$_2$-O-CO- methylenes, one corresponding to a reacted **C2** unit connected to **PS** (C^{1bs}) and the other one to an oxydiethylene end group of **PS** connected to a reacted **C2** unit (C^{3sb}). New methylene peaks at 36.9 and 27 ppm are assigned to C^{2bs} and C^{4bs}. Similar observations are made on the **PA/C1/PS** system, showing that in both cases the expected reaction between **PS** and **CC** end groups has taken place. The secondary peaks at 157 ppm disappear in the spectrum of the final copolymer.
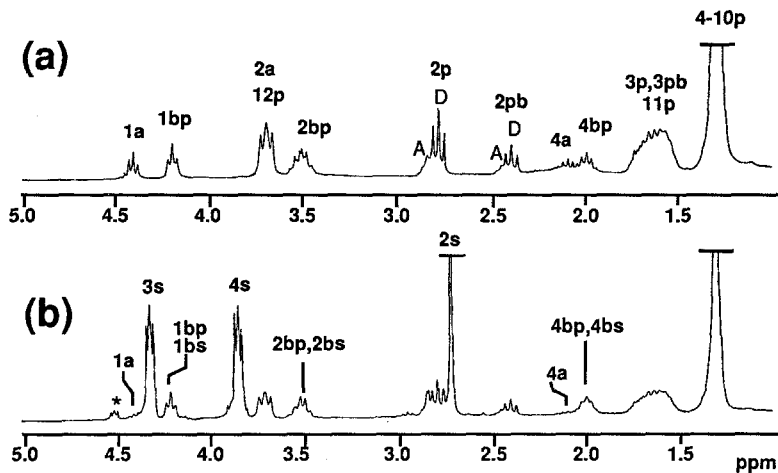
Figure 2 : ^{1}H NMR spectra (250 MHz, TFA/CDCl$_3$, ref. TMS) of (a) **PA/C2** and (b) **PA/C2/PS**. See Fig. 1 for atom numbering and text for *.

Study of reaction by ^{1}H NMR

The compounds obtained after the first step have been analyzed by ^{1}H NMR. Due to HFIP peak overlapping, the solvent used here was a trifluoroacetic anhydride (TFA)/CDCl$_3$ mixture. Trifluoroacetic anhydride allows polyamide solubilisation by reaction with NH groups. This reaction liberates trifluoroacetic acid, which in turn reacts with oxazoline or oxazine end groups. These end groups are therefore detected as -CH$_2$-O-CO-CF$_3$ groups in the ^{1}H NMR spectra.

The spectrum of **PA/C2** is given in fig. 2a. The three methylenes of reacted oxazine moieties give resonances at 1.98, 3.50 and 4.19 ppm (H^{1bp}, H^{2bp}, H^{4bp} respectively), while resonances corresponding to unreacted oxazine end groups appear at 2.08 and 4.40 ppm (H^{4a} and H^{1a} respectively). The reaction is also evidenced by the disappearance of the resonance of the methylene in α position to COOH at 2.6 ppm replaced by the resonance of -CH$_2$-COO- methylene at 2.4 ppm (H^{2pb}). The same holds for the modification of **PA** by **C1**.

After the addition of **PS**, the resonances corresponding to unreacted **C2** end groups disappear almost completely (Fig. 2b). However the presence of residual **C2** moieties can be noticed (H^{1a}). The triplet at 4.5 ppm (starred peak) has been tentatively assigned to the H^{3sb} ester methylene of units connecting **PS** and **PA** block.

Study of reaction by carboxyl group titration

At the end of the first step, the carboxy content of **PA/C1** and **PA/C2** is below 0.05 mmol.g^{-1}. The variations of the carboxy concentration during reactions between **PA/C1** or **PA/C2** and **PS** (second step) are given in fig. 3. There is no significant difference in the reactivity of the two coupling reagents. Reaction rate is lower than observed during the synthesis of the corresponding homopolymers (6). As a consequence, the final carboxy
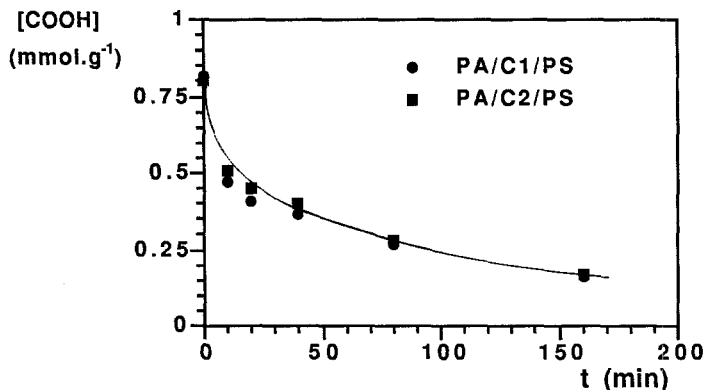
Figure 3 : Stoichiometric bulk reaction between **PS** and **C1**- or **C2**-terminated **PA** at 200°C. Variations of carboxyl group concentration ([COOH] (mmol.g^{-1}) versus time.

content is relatively high, 0.16 mmol/g for both reactions. From NMR study, both **CC** and $\overline{\text{COOH}}$ end groups are present. Assuming that the concentration of these groups is same, $\overline{M_n}$ is close to 6000, lower than obtained using bisoxazolones and amino-terminated oligomers (2).

Thermal properties of the block-copolymers

The TGA study shows that the thermal stability of block copolymers is intermediate between those of the two starting oligomers (Table 1). The results of DSC study of the starting **PA** and **PS**, and of block copolymers are given in table 1. Block copolymers exhibit both a low temperature glass transition, corresponding to the polyester phase, and a high temperature melting point corresponding to the polyamide phase, showing a phase separation between the two blocks. The T_g of **PS** block increases with respect to the starting oligomer. This may be assigned to some compatibilization of polyamide in the polyester phase. On the other hand, melting points are very close to that of starting **PA**. The melting enthalpy of a high molar mass **PA/CC** polymer is close to 30 J/g (6). From the mass fraction in the final block copolymer, melting enthalpy should be 15 J/g, value which is close to the experimental one.

Table 1 : Thermal characterization of α,ω-dicarboxy poly(2,2'-oxy-diethylene succinate) (**PS**), α,ω-dicarboxy poly-amide 12 (**PA**), and of their reaction products with **C1** and **C2** :
$T_{5\%}$: 5% mass loss temperature (TGA), T_g, T_m, ΔH_m: melting and glass transition temperatures and melting enthalpy (DSC).

Sample	$T_{5\%}$ (°C)	T_g (°C)	T_m (°C)	ΔH_m (J/g)
PS	266	-23	-	-
PA	350	-	154	47
PA/C1/PS	316	-8	154	17
PA/C2/PS	335	-5	154	11

Conclusion

The preparation of polyamide-polyester block copolymers can be carried out using a two-step coupling reaction, involving a second step with reaction between oxazoline-terminated polyamide and a carboxy-terminated polyester at 200°C. The DSC study shows the existence of a phase separation between polyamide and polyester phase, and therefore indicates that the randomization of PA and PS blocks by ester/amide interchange does not take place. Reaction kinetics is slower than previously observed on the **PS** homopolymer : 90% conversion is reached only after 160 min reaction, and both oxazoline and carboxy end groups can be detected at this reaction time. Consequently, the molar mass of resulting block copolymers is relatively low. It is clear that higher conversions and higher molar masses would be obtained at temperatures higher than 200°C. This would, however, exclude the use of aliphatic polyesters which generally become unstable above this temperature.

References

1   M. Acevedo and A. Fradet, *J. Polym. Sci., Part A: Polym. Chem.* **31**, 817 (1993).
2   M. Acevedo and A. Fradet, *J. Polym. Sci., Part A: Polym. Chem.* **31**, 1579 (1993).
3   H. Inata and S. Matsumura, *J. Appl. Polym. Sci.* , **30**, 3325 (1985).
4   H. Inata and S. Matsumura, *J. Appl. Polym. Sci.* , **32**, 5193 (1986).
5   T. Loontjens, W. Belt, D. Stanssens and P. Weerts, *Polym. Bull.* **30**, 13 (1993).
6   A. Douhi and A. Fradet, *J. Polym. Sci., Part A: Polym. Chem.* **33**, 691 (1995).
     Erratum : in this ref PS corresponds to poly(2,2'-oxydiethylene *succinate*) and not *adipate*, as erroneously mentioned in abstract and introduction.
7   *Ger. Pat.* DE 2,153,513, October 27, 1971 ; Bayer-A.-G., inv : H. Appel
8   H. Wenker, *J. Am. Chem. Soc.* **60**, 2152 (1938).
9   P. J. Flory, *J. Am. Chem. Soc.* **58**, 1877 (1936).
10   L. H. Peebles Jr, *Macromolecules* **7**, 872 (1974).
11   F. Lopez-Serrano, J. M. Castro, C. W. Macosko and M. Tirell, *Polymer* **21**, 263 (1980).