Preparation and structure of polyether-block containing polymers

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Abstract: Block-copolymers were prepared by direct polycondensation of functional oligomers or by polycondensation of a functional oligomer with the precursors of another block. Three series of copolymers were prepared and characterized: poly(polyamide 12-*block*-copolyether)s, Polyisobutylene-*block*-polyoxyethylene-*graft*-polyoxyethylene and poly(semi-aromatic polyester-*block*-polyoxytetra methylene)s. The functional oligomers and the corresponding copoly-condensates were characterized by SEC, infra-red spectroscopy, mass spectrometry, ^{1}H and ^{13}C NMR (solution and solid state). Their thermal properties were analyzed and the extent of the segregation in poly(polyester semi-aromatic-*block*-polyoxytetramethylene)s was studied through visco-elastic properties.

INTRODUCTION

A large part of the activity of our laboratory is devoted to block copolycondensates (ref. 1-16). We use three main methods:

(i) direct polycondensation of a,w-difunctional oligomers:
X-[Oligomer 1]-X + Y-[Oligomer 2]-Y Æ ~X'-[Block 1]-X'Y'-[Block 2]-Y'~

(ii) polycondensation of an a,w-difunctional oligomer with the precursors of another block:
X-[Oligomer 1]-X + A-A + B-B Æ ~X'-[Block 1]-X'Y'-[Block 2]-Y' ~
        with Y'-[Block 2]-Y' is A'A'B'B'-[A'A'B'B']-A'A'

(iii) oligomer-coupling reactions:
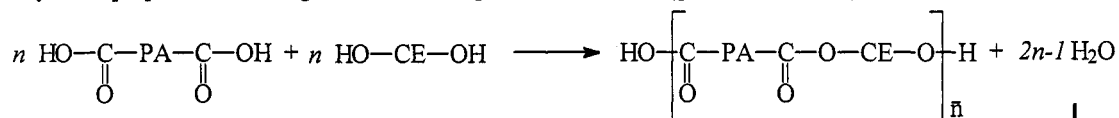X-[Oligo 1]-X + Y-[Oligo 2]-Y + C-C Æ ~X'-[Block 1]X'C'C'Y'[Block 2]-Y'~

This lecture concerns the following copolymers:

> Poly(polyamide 12-*block*-copolyether)s
> Poly(polyisobutylene-*block*-polyoxyethylene-*graft*-polyoxyethylene)s
> Poly(semi-aromatic polyester-*block* polyoxytetramethylene)s

SYNTHESES OF THE BLOCK-COPOLYMERS

Poly(polyamide-*block*-copolyether)s

They were prepared according to the following reaction scheme (general method I):

$$n \ \text{HO}-\underset{\underset{O}{\|}}{C}-\text{PA}-\underset{\underset{O}{\|}}{C}-\text{OH} + n \ \text{HO}-\text{CE}-\text{OH} \longrightarrow \text{HO}-\left[\underset{\underset{O}{\|}}{C}-\text{PA}-\underset{\underset{O}{\|}}{C}-\text{O}-\text{CE}-\text{O}\right]_{\bar{n}}-\text{H} + 2n\text{-}1 \ \text{H}_2\text{O}$$
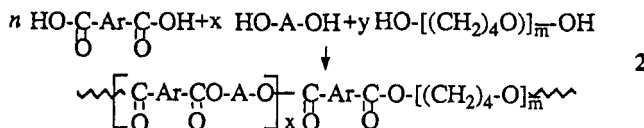
where CE is the copolyether-block

Copolyethers

We used Synperonic® (ICI) and Pluronic® (BASF). In principle, they are triblock-copolymers (POE-POP-POE) but in fact they are mixtures of triblock and biblock copolymers and polyoxypropylene; however all of them are difunctional. Their $\overline{\text{Mn}}$ (Table 1) was obtained by SEC, MS, and ^{1}H NMR and the values obtained by these different techniques are in good agreement. Their composition and structure were essentially determined by ^{1}H NMR and ^{13}C NMR.

TABLE 1. Characteristics of the copolyethers. [OE] and [OP] are the concentrations of oxyethylene and oxypropylene units; pri-OH and sec-OH are the concentrations of the primary and secondary end hydroxy-groups of the oligomers.

| Oligomers	$\overline{Mn}$	^{1}H NMR %[-OE]/[OP]	%-pri-OH	%-sec-OH
Synperonic L-35	1920	1.26	90	10
Synperonic L-44	2205	1.09	85	15
Synperonic L-43	1840	O.77	80	20
Pluronic 4300	1925	0.65	80	20
Synperonic L-42	1570	0.26	75	25
Synperonic L-61	1950	0.23	60	40
Synperonic L-31	1090	0.25	50	50
Pluronic 6100	1740	0.14	45	55
Pluronic 3100	1095	0.16	35	65

Poly(semi-aromatic polyester-*block*-polyoxytetramethylene)s

They were prepared according to the following reactionnal scheme (general method II):

$$n \ HO\text{-}\underset{O}{\overset{}{C}}\text{-}Ar\text{-}\underset{O}{\overset{}{C}}\text{-}OH + x \ HO\text{-}A\text{-}OH + y \ HO\text{-}[(CH_2)_4O)]_{\overline{m}}\text{-}OH$$

$$\downarrow \qquad\qquad\qquad 2$$

$$\sim\sim\left[\underset{O}{\overset{}{C}}\text{-}Ar\text{-}\underset{O}{\overset{}{C}}O\text{-}A\text{-}O\right]_x \underset{O}{\overset{}{C}}\text{-}Ar\text{-}\underset{O}{\overset{}{C}}\text{-}O\text{-}[(CH_2)_4\text{-}O]_{\overline{m}}\sim\sim$$

Six semi-aromatic copolymers were studied; in this lecture only the results relative to three of them are reported; they correspond to the scheme **3**.
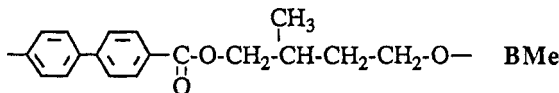
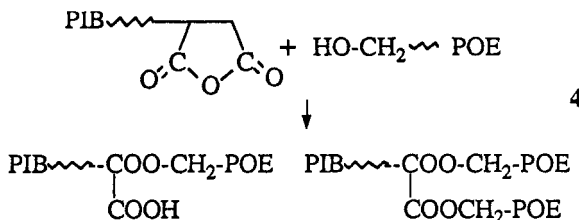When A is $(CH_2)_6$ Ar can be:
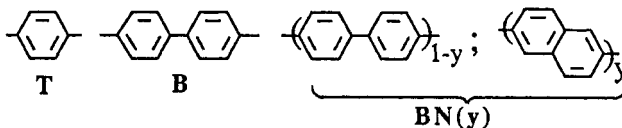
y is the contribution of N in Ar (mol%)

3

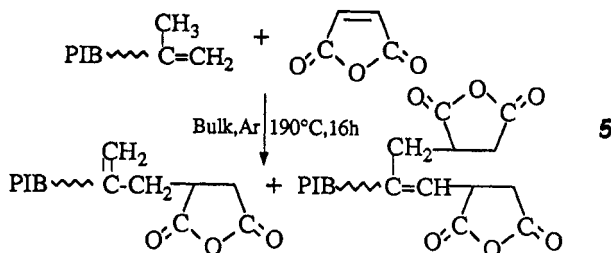The block-polyester can be also:

BMe

Polyisobutylene-*block*-polyoxyethylene-*graft*-polyoxyethylene

They were prepared according to the following reactionnal scheme (general method I):

4

PIB$\sim\sim$-$\underset{\underset{COOH}{|}}{C}OO\text{-}CH_2\text{-}POE$ PIB$\sim\sim$-$\underset{\underset{COOCH_2\text{-}POE}{|}}{C}OO\text{-}CH_2\text{-}POE$

a-monoanhydride and a,a'-dianhydride oligoisobutylene

a-chloro oligoisobutylenes were prepared according to Nguyen and Kennedy (ref. 17) and improved by Rodrigues (ref. 18); they were dechlorinated, giving a-isopropenyl oligoisobutylenes, then reacted with maleic anhydride; these reactions were particularly studied by Tessier (ref. 19,20).

$$\text{PIB}\sim\sim \underset{\displaystyle \underset{CH_2}{|}}{C}=CH_2 \quad + \quad \text{(maleic anhydride)} \qquad \xrightarrow[\text{Bulk,Ar}]{190°C,16h} \qquad \text{PIB}\sim\sim C-CH_2\text{...} \quad + \quad \text{PIB}\sim\sim C=CH\text{...} \qquad \mathbf{5}$$

CHARACTERIZATION OF THE BLOCK COPOLYMERS

Poly(polyamide-*block*-copolyether)s

The block-copolymer prepared from L-35 exhibits the following characteristics: [h] =1.3 dL.g^{-1} and $\overline{Mn}$ is above 20000. The functionnal end group signals are no longer observed in the corresponding ^{1}H NMR spectrum and those of the methylene preceding (2.35 ppm) and following (4.25 ppm) the ester group confirm that the polycondensation took place. Solid state NMR spectroscopy provides interesting information on several copolymers.

The crystalline domains of the precursory oligoamide and of the polyamide-blocks are g monoclinic structures which is confirmed by X-ray diffractometry. The polyether-block of a poly[polyamide-*block*-polyoxytetramethylene] is amorphous when its Mn is 1000 and partially crystallized when Mn is 2000.

The polyether-block of a poly[polyamide-*block*-polyoxyethylene] contains a crystalline phase and an amorphous one. On the other hand the polyether blocks of poly[polyamide-*block*-polyoxypropylene] and of poly[polyamide-*block*-copolyether] are amorphous.Their thermal properties are reported in table 2.
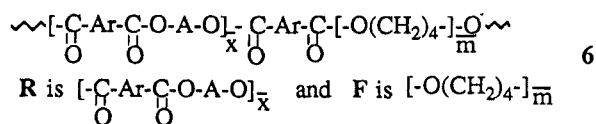
TABLE 2. Thermal properties of poly[polyamide-*block*- polyether]s. Tg, Tm, Tr (°C); ÆHm, ÆHr (J.g^{-1}) are respectively glass transition, melting and crystallisation temperatures, melting and crystallisation enthalpies.

Polymer $\overline{Mn}$	Heating					Cooling	
	TgPE	TmPE	ÆHmPE	TmPA	ÆHmPA	TrPA	ÆHrPA
PA12DC (2100)	-	-		166	75	138	59
POE (1015)	-	47	136				
POP (928)	-52	-	-				
PTOM (1075)	-83	27	107				
PA-POE	-40	7	5	166	37	132	39
PA-POP	-47	-	-	161	38	133	37
PA-POTM	-50	11	3	162	33	131	35
L31	-55	-	-				
L35	-52	28	15				
PA-L31	-44			164	36	135	36
PA-L35	-44			168	30	135	31

TmPA, ÆHmPA, TrPA and ÆHrPA little depend on polyether nature and $\overline{Mn}$. The polyether block Tg is above that of the precursor.

Poly(semi-aromatic polyester-*block*-polyoxytetramethylene)s

Their structure is given by formula **6**:

$$\sim\!\!\sim[\text{-C-Ar-C-O-A-O}]\text{-}\underset{x}{}\text{C-Ar-C-[-O(CH}_2)_4\text{-]-O}\!\sim\!\!\sim$$

$$\text{R is } [\text{-C-Ar-C-O-A-O}]_{\overline{x}} \quad \text{and} \quad \text{F is } [\text{-O(CH}_2)_4\text{-}]_{\overline{m}}$$

6

Ar and A structures are given in scheme **3**. The $\overline{\text{Mn}}$ of **R** blocks (^{1}H NMR) is given in table 3. The $\overline{\text{Mn}}$ of **F** is 2100 and their thermal and mesomorphic properties are reported in table 4

TABLE 3. $\overline{\text{Mn}}$ of the blocks in the copolycondensates. Theoretical values are given in brackets. w is the weight percentage of **F** in **R-F**

Copolymer	x	$\overline{\text{Mn}}$ of **R**	F(w%)
T-F	31 (28)	7650 (6860)	23 (25)
B-F(	20 (22)	6440 (7092)	27 (25)
BN(26)-F	23 (22)	7365 (7070)	24 (25)
BMe-F	15 (15)	4670 (4730)	34 (33)

TABLE 4. Thermal and mesomorphic properties of the copolymers. Ti is isotroposition temperature and ÆT is the temperature mesomorphic domain.

Polymer	Tg,F	Tm,F	Tm,R	Ti	ÆT	Mesophase
F	-83	35	-	-	-	-
T	-	-	147	-	-	-
T-F(34)	-74	17	144	-	-	-
B	-	-	214	241	27	Smectic A
B-F(27)	-76	28	223	231	8	Smectic A
B-F(50)	-78	25	224	233	9	Smectic A
BN(25)	-	-	192	227	35	Smectic A
BN(26)-F(24)	-77	29	197	209	12	Smectic A
BMe	-	-	214	232	18	Nematic
BMe-F(26)	-81	26	215	231	16	Nematic

We compared the segregation extent when Ar is benzenic ring (the copolycondensate is not mesomorphic) and when the copolycondensate exhibits mesomorphic properties **B,BN,BMe**); in this purpose their viscoelastic properties were studied (table 5).

TABLE 5. Temperature TE"max (°C; 1 Hz; 10°C min^{-1}).

Copolymer	TE"max	Copolymer	TE"max	Copolymer	TE"max
T-F(23)	-4	**T-F(34)**	-37	**T-F-(43)**	-63
B-F(27)	-51	**B-F(33)**	-53	**B-F(50)**	-46
BN(26)-F(24)	-46/-20	**BN(30)-F(34**	-46/-20	**BN(28)-F(49)**	-47/-20
BMe-F(20)	- 49	**BMe-F(26)**	-55	**BMe-F(34)**	-56

The rheological properties in the melt were studied. With **T** the solid/liquid transition is characteristic of an isotropic material: G" is always far above G' and its value is proportional to the pulsation (w) whatever T. On the other hand with **B** or **BN** G' is above G" when T is below Tm showing it is an elastic solid material.

When Tm <T <Ti, G' and G" are very closed and rapidly decrease with T increasing which is characteristic of a smectic phase; in this domain G" is roughly proportional to $w^{0.5}$. When T > Ti, the corresponding isotropic liquid is characterized by G" > G'. The nematic state of **B-Me**-copolymers is characterized by a weak decrease of G' and G" when T increases.

Polyisobutylene-*block*-polyoxyethylene-*graft*-polyoxyethylene

The reaction product of anhydride-oligoisobutylenes with a-hydroxy-polyoxyethylene (**7**) was characterized by infra-red spectroscopy, mass spectrometry and SEC.
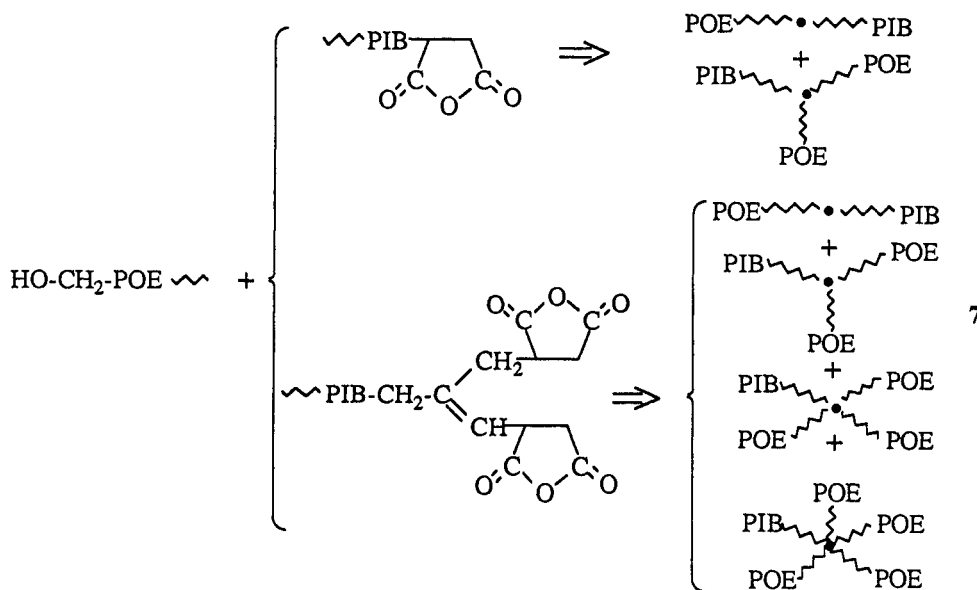
characteristics do not depend on the structure of the oligoisobutylene. When the $\overline{Mn}$ of POE is 815 Tg is -64°C, crystallisation temperature is -45.5°C and Tm is 24.5 °C ; when it is 2015 Tg is -45°C, Tm is 49 °C. Some of their amphiphilic properties were determined and particularly cloud-point and surface-tension. Their water solubility is high due to the fact that the hydrophobic block has a low molar mass; they have a classical behaviour of non-ionic surfactant.

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