Polymer Bulletin 6, 477–484 (1982)

Polymer Bulletin

α,ω- Bifunctional Poly(p-phenylene sulfide) Oligomers
2. Segmented Copolyesters

G. Daccord and B. Sillion

Institut Français du Pétrole C.E.D.I., BP No. 3, F-69390 Vernaison, France

Summary

This paper describes the synthesis and properties of copolyesters of poly(butyleneisophtalate) (PBI) and poly(butyleneterephtalate) (PBT) containing poly(p-phenylenesulfide) (PPS) segments of varying lengths. The products were analysed mainly by NMR and DSC techniques, which enabled us to determine the miscibility limit of PPS segments in the amorphous zone of the polyester and to compare it with a theoretical value calculated beforehand.

Introduction

Some block copolymers were studied with the aim of showing that the phenomenon of phase separation which may appear is a fonction of the length of each block and of the solubility of the different blocks, in one another.

The interest of these block copolymers lies in their properties:

- physical reticulation when phase separation occurs, which gives rise to thermoplastic elastomers.
- modification of the interfacial tension of the two blended polymers, which allows their compatibilisation and produces materials with better properties, particularly mechanical (RIESS et al. 1968 and 1980, JEROME et al. 1980, OLABISI et al. 1979).

Work is generally conducted on anionic polymers and much more rarely on polycondensed polymers.

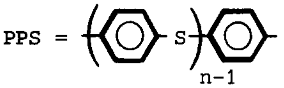
In this article, we are interested in segmented copolycondensed polymers in the vicinity of their demixing into two distinct phases. We describe the synthesis of segmented copolyesters from α,ω-bifunctional oligomers of PPS having a well defined length, and we analyse the properties of the materials mainly to determine the limit of solubility of PPS segments in the polymer and its relation to their length.

These polymers conform to the general following formula:

0170-0839/82/0006/0477/$01.60

$$\left\{ \left[\text{O-CO-Ar-COO}(\text{CH}_2)_4 \right]_m \left[\text{X-CO-PPS-CO-X}(\text{CH}_2)_4 \right]_p \right\}_q$$

X = -O- or $-\text{NH-CH}_2\text{-CH}_2\text{-O-CO-Ar-COO-}$



n = 2, 4, 6 or 11,3

(n being the number of p-phenylene nuclei)

Synthesis

The copolyesters were prepared from α,ω-diester ($\underline{1}_n$) or α,ω-diol ($\underline{2}_n$) PPS oligomers previously described (DACCORD et al. 1981), either by polyesterification with a methyl terephtalate or isophtalate and a diol (method I), or by reaction with a previously prepared polyester (method II).

Method I : Using methyl terephtalate or isophtalate and 1,4 butanediol, we condensed the diester oligomers $\underline{1}_n$ according to equation 1 and the diol oligomers $\underline{2}_n$ according to equation 2.

$$\text{ROCO-}\underset{\underline{1}n}{\text{PPS}}\text{-COOR} + \text{CH}_3\text{OCO-Ar-COOCH}_3 + \text{HO}(\text{CH}_2)_4\text{OH} \longrightarrow$$
$$\left\{ \left[\text{OCO-Ar-COO}(\text{CH}_2)_4 \right]_m \left[\text{OCO-PPS-COO}(\text{CH}_2)_4 \right]_p \right\}_q$$

(Eq. 1)

$$\text{HOCH}_2\text{CH}_2\text{NHCO-}\underset{\underline{2}n}{\text{PPS}}\text{-CONHCH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{OCO-Ar-COOCH}_3 + \text{HO}(\text{CH}_2)_4\text{OH} \longrightarrow$$
$$\left\{ \left[\text{OCO-Ar-COO}(\text{CH}_2)_4 \right]_m \left[\text{OCO-Ar-COOCH}_2\text{CH}_2\text{NHCO-PPS-CONH}_2\text{CH}_2\text{CH}_2 \right]_p \right\}_q$$

(Eq. 2)

Method II : Here, PPS oligomers (either diester as in equation 3 or diol as in equation 4) are incorporated into a polyester:

$$\text{HO}\left[(\text{CH}_2)_4\text{OCO-Ar-COO} \right]_m (\text{CH}_2)_4\text{OH} + \text{ROCO-}\underset{\underline{1}n}{\text{PPS}}\text{-COOR} \longrightarrow$$
$$2\ \text{ROH} + \left\{ \left[\text{OCO-Ar-COO}(\text{CH}_2)_4 \right]_m \left[\text{OCO-PPS-COO}(\text{CH}_2)_4 \right]_p \right\}_q$$

(Eq. 3)

$$\text{HO}\left[(\text{CH}_2)_4\text{OCO-Ar-COO} \right]_m (\text{CH}_2)_4\text{OH} + \text{HOCH}_2\text{CH}_2\text{NHCO-}\underset{\underline{2}n}{\text{PPS}}\text{-CONH}_2\text{CH}_2\text{CH}_2\text{OH} \longrightarrow$$
$$\text{HO}(\text{CH}_2)_4\text{OH} + \left\{ \left[\text{OCO-Ar-COO}(\text{CH}_2)_4 \right]_m \left[\text{OCO-Ar-COOCH}_2\text{CH}_2\text{NHCO-PPS-CONHCH}_2\text{CH}_2 \right]_p \right\}_q$$

(Eq. 4)

All these transesterifications and polycondensations are catalysed by butyltitanate and are conducted at a temperature above the melting temperature of the products up to 280°C.

All of the prepared products are listed in Table I.

Characterization and study of the properties of the copolymers.

Study of the structure by chloroform extraction.

The effectivness of the incorporation of PPS segments is demonstrated by chloroform extraction, a PBI solvent, especially in the case of polymers prepared from the insoluble PPS segments 1_6 and $2_{11,6}$. In the first case, all the polymers 5A, B and C are totally soluble. In the second, by continuous hot chloroform extraction, we obtain a soluble fraction (7A1) containing p-phenylenesulfide units (IR: absorption band at 820 cm^{-1}) and an insoluble fraction (7A2) containing isophtalate units (IR: bands at 1720 and 720 cm^{-1}).

Analysis of the composition by NMR

By integrating the different multiplets of the part of the spectrum corresponding to aromatic protons, we can calculate an approximative value of the molar composition. Figure 1 gives the example of product 4A (band c corresponds to terephtalate units, an impurity in the isophtalate). The results given in Table 1 show fairly good agreement between the theoretical molar composition and the experimental one.

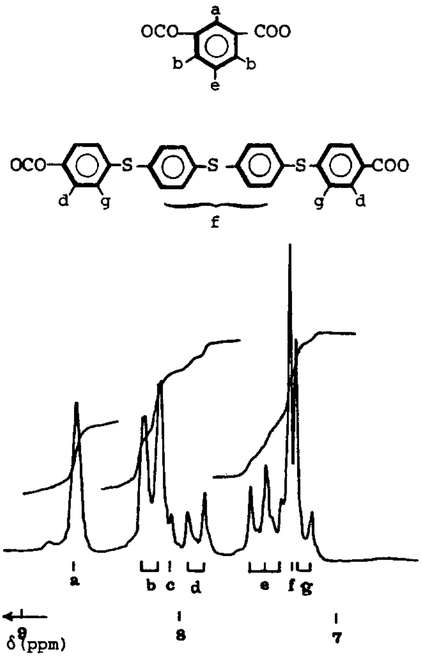
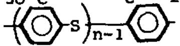


Fig. 1 - Part of the NMR spectrum of the 4A copolymer corresponding to aromatic protons (solvent $CDCl_3$ reference TMS)

Réf.	Starting products[a]	Synthetic method	(dl/g)[b]	Composition molar[c] theoretical	Composition molar[c] experimental (RMN)	weight[d] %	DSC (°C) T_g	DSC (°C) T_{LT}[e]	DSC (°C) T_{HT}
3	DMI + BD + $\underline{1}_2$	I	0.7	1/1	0.8/1	33	16	-	86
4A	DMI + BD } + $\underline{1}_4$	I	0.9	8/1	-	17.4	31	variable	104
4B	PBI }	II	0.6	30/1	-	10	26	variable	128
5A	PBI }	II	0.4	16/1	15-17/1	16.7	22	variable	133
5B	DMI + BD } + $\underline{1}_6$	I	0.4	30/1	27/1	8.4	-	variable	135
5C	PBI }	II	0.8	66/1	40-80/1	4.8	23	variable	133
6A	DMI + BD } + $\underline{2}_4$	I	insoluble	4/1	insoluble	29	50	-	-
6B	DMI + BD }	I	0.7	20/1	10.5-14/1	8.2	30	variable	115
							25[f]	95[f]	200[f]
7A	DMI + BD } + $\underline{2}_{11.3}$	I	0.2[b]	-	-	22	43[g]	-	245[g]
7B	PBI }	II	insoluble	-	-	20	26	120	280
8	DMT + BD + $\underline{1}_4$	I	insoluble	4/1	-	28	40	variable	165
9	DMT + BD + $\underline{2}_4$	I	0.4	4/1	2.8/1	29	62	variable	167
10A	DMT + BD } + $\underline{2}_{11.3}$	I	insoluble	-	-	10	40	212	278
10B	PBT }	II	insoluble	-	-	10	41	208	281

a - DMI = dimethylisophtalate ; DMT = dimethylterephtalate ; BD = 1,4-butanediol ; PBT = poly(butyleneisophtalate)

b - 0.5% solution in o-chlorophenol at 30°C c - fraction : number of polyester units/number of PPS oligomers

d - theoretical percentage of segments 

e - variable = dependent on annealing conditions f - chloroform soluble fraction (7A1)

g - chloroform insoluble fraction (7A2)

TABLE I - Caracteristics and properties of prepared copolyesters

DSC study and discussion

The copolyesters show a glass transition and generally two first-order transitions. These melting transitions for products 7 and 10 are situated in the vicinity of the melting temperature of each of the homopolymers (PBI: Tg = 21°C, T_M = 125° ; PBT: Tg = 36°, T_M = 213° ; PPS: Tg = 87°, T_M = 260°).

For the other copolymers, the position of the transition occuring at low temperature (T_{LT}) is heavily dependent on the thermal history of the studied sample and on the heating rate ; the position of the high temperature transition (T_{HT}) is independent of these parameters. Figures 2, 3 and 4 illustrate this behaviour in products 4B and 9.

The variations in glass temperature inform us on the possible phenomenon of demixing of PPS segments in the PBI amorphous phase: we observe an important increase in Tg for 4A but very little for 5. With the PBT, this effect is negligible for 8 but considerable for 9 just as for 6A and B. These anti-plastification-like effects in oligomers 1_4 and 2_4 demonstrate the miscibility of these PPS segments with polyester ; this effect is logically greater in the diol oligomers which include amide functions.

For the longest oligomers (products 7 and 10), the two melting temperatures described above show a sharp phase separation.

Discussion of the melting temperatures of the other copolymers requires a more detailed study. Multiple melting transitions in a semicrystalline polymer may be due to the annealing conditions, as this has been demonstrated particularly for poly(ethylene-terephtalate) (HOLDSWORTH 1971), for polyamides (ROBERTS 1969 ; FIELDING-RUSSELL et al. 1970) and for isotactic polystyrene (LEMSTRA 1972).

An invariable high-temperature transition is generally observed but its surface depends on the heating rate ; low-temperature transition varies with annealing conditions. A recrystallisation phenomenon is said to occur during the recording of the thermogram(HOLDSWORTH et al. 1971 ; ROBERTS 1969 and 1970 ; FIELDING-RUSSELL et al. 1970 ; COPPOLA et al. 1975).

The observed behaviour of copolyesters is qualitatively the same as the one described in the litterature for semicrystalline polymers ; meanwhile, when in the case of isotactic polystyrene, the experiment confirms the theory which predicts that the curve $T_{LT} = f(T_C)$ is a straight line intersecting the bisector at the thermodynamic melting point (LEVY et al. 1972), in these polymers the variation of T_{LT} with the annealing temperature T_C (Fig. 4) so in homopolymers PBI and PBT as in the copolyesters is linear and parallel to the bisector. As far as we know, this behaviour has not yet been described.

The lowering of the HT melting point of the products containing the greatest percentage of PPS segments (4A, 6A, 8 and 9) confirms their block structure. Indeed it can be interpreted as a consequence of the decrease in the mean length of polyester blocks, hence decrease in the maximum width of the crystallites and in their melting temperature.

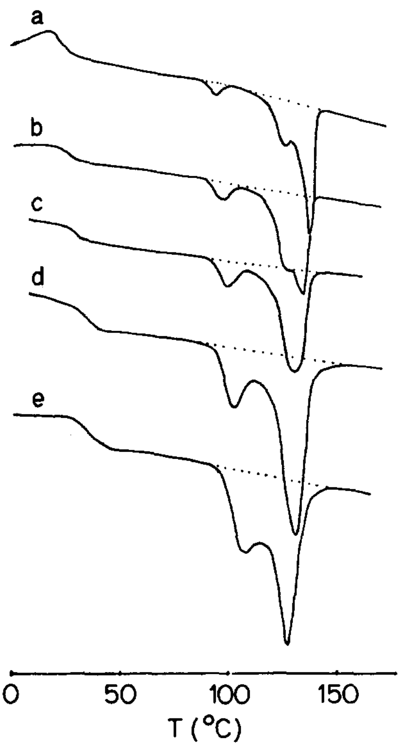


Fig. 2 - Evolution of the thermograms of 4_B annealed at 70°C for 5 h with the heating rate : a = 2°/mn - b = 5°/mn - c = 10°/mn - d = 20°/mn - e = 50°/mn.

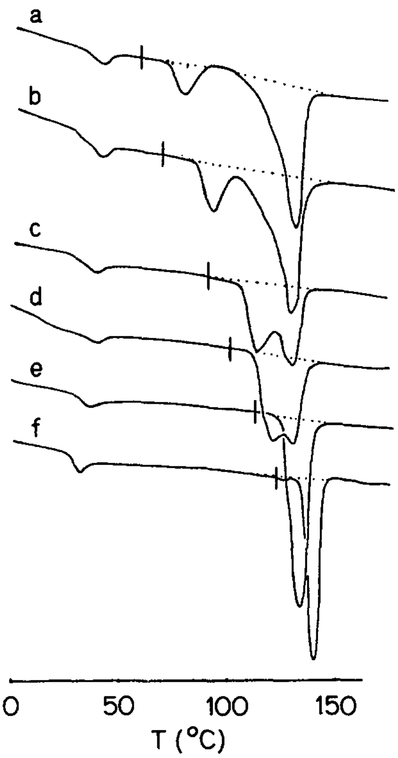


Fig. 3 - Evolution of the thermograms of 4_B with the annealing temperature (annealing time = 1 h, heating rate = 10°/mn - a = 60°C - b = 70° - c = 90° - d = 100° - e = 110° - f = 120°

The increase in the PPS segment content also has an effect on the relative surface of the LT transition, which increases in relation to the HT transition, other conditions being unchanged.

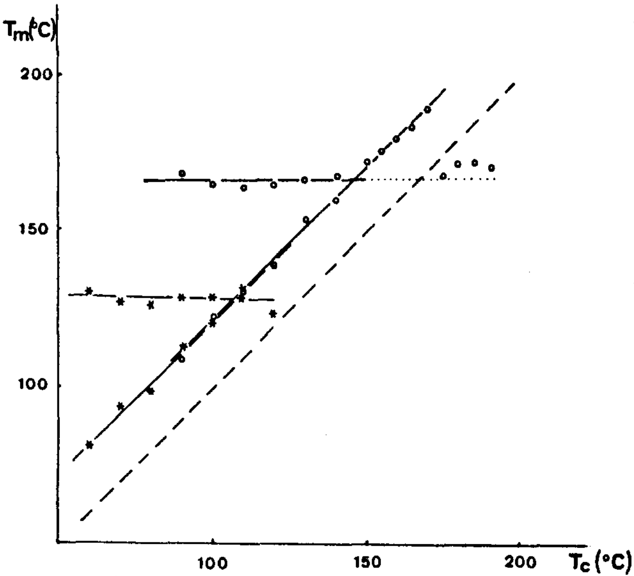


Fig. 4 - Evolution of the melting temperatures of products 4A (circles) and 9 (stars) with the annealing temperature. Heating rate = 10°/mn - Annealing time = 4h for 4A and 80 mn for 9. The temperatures are measured at the top of the transitions. Dashed line: $T_m = T_C$

Conclusion

The miscibility limit of two polymers can be theoretically approximated by using the methodology described by S. Krause (PAUL et al. 1978): first the solubility parameters δ are calculated for each polymer, then the coefficient of mutual interaction χ. The numerical values for the system PBT-PPS which were obtained are: $\delta_{PBT} = 10.9$; $\delta_{PPS} = 12.0$ and $\chi = 0.20$.

The critical polymerization degree after which total miscibility will not occur is such that:

$$\frac{1}{2}\left[(\bar{dp}_{PPS})^{-\frac{1}{2}} + (\bar{dp}_{PBT})^{-\frac{1}{2}}\right]^2 = \chi$$

Thus, for a mean weight of PBT of 10^4 $\bar{dp}_{PPS} = 4.3$

The analysis which we have just made shows that the miscibility limit of PPS oligomers corresponds to a polymerization degree of between 4 and 6, which is in good agreement with the theoretical prediction.

Experimental

NMR spectra wera recorded with a Brucker WP-80 instrument (solvent $CDCl_3$, reference TMS).
DSC diagrams were recorded with a Dupont 990 instrument with a DSC 910 unit. Annealing was carried out in the cell. The heating rate, except where it is advisable was 10°/mn.

Synthesis of the polyesters

The starting products are commercial and were purified before use. All the products were prepared according to similar operating modes.

Method I - The starting products are kept in a polymerization reactor with a 100% excess of 1,4-butanediol and 0.3% of butyltitanate. The reactor is heated to 250°. After a quantity near the stoechiometry of methanol has been collected, the pressure is gradually lowered to 0.1 torr and the temperature increased to 280°. After 1 h the melted product is poured into methanol, filtered and dried.

Method II - Identical to method I, except that the initial step of transesterification at ambient pressure is suppressed.

References

COPPOLA, G., FABRI, P., PALLESI, B., ALFONSO, G.C. and DONDERO, G.: Makromol. Chem. 176, 767 (1975)

DACCORD, G. and SILLION, B.: Polymer Bulletin 4, 459 (1981)

FIELDING-RUSSEL, G.S. and PILLAI, P.S.: Makromol. Chem. 135, 263 (1970)

HOLDSWORTH, P.J. and TURNER-JONES, A.: Polymer 12, 195 (1971)

JEROME, R. and FAYT, R.: L'actualité Chimique sept. 1980, 21

LEMSTRA, P.J.: J. Pol. Sci. A2 10, 823 (1972)

LEVY, A. and NOEL, C.: J. Chim. Phys. 69, 875 (1972)

OLABISI, O., ROBESON, L.M. and SHAW, M.T.: Polymer-Polymer Miscibility, New-York: Academic Press 1979

PAUL, D.R. and NEWMAN, S.: Polymer Blends, Vol. 2, New-York: Academic Press 1978

RIESS, G., KOHLER, S. and BANDERET, A.: Eur. Pol. J. 4, 173 and 187 (1968)

RIESS, G., GAILLARD, P. and OSSENBACH-SAUTER, M.: Makromol. Chem., Rapid Comm. 1, 771 (1980)

ROBERTS, R.C.: Polymer 10, 119 (1969)

ROBERTS, R.C.: J. Pol. Sci., Pol. Letters Ed. 8, 381 (1970)

Received January 22, accepted January 24, 1982