

Molecular design of multicomponent polymer systems*: emulsifying effect of poly(α -methylstyrene-*b*-methyl methacrylate) in poly(vinylidene fluoride)/poly(α -methylstyrene) blends

T. Ouhadi, R. Fayt, R. Jerome and Ph. Teyssey

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman, 4000 Liège, Belgium

(Received 22 October 1985; revised 11 March 1986)

A preliminary evaluation of the morphology and mechanical behaviour of poly(vinylidene fluoride)/poly(α -methylstyrene) blends provides clear evidence for the important emulsifying effect of a poly(α -methylstyrene-*b*-methyl methacrylate) copolymer. Moderate amounts (2 wt%) of the copolymer greatly improve phase dispersion and interfacial adhesion and also very significantly increase Young's modulus and ultimate tensile strength of the blends; even a synergy in the strength is observed.

(Keywords: poly(vinylidene fluoride)/poly(α -methylstyrene) blends; poly(α -methylstyrene-*b*-methyl methacrylate) copolymer; emulsifying effect; polymeric emulsifiers)

INTRODUCTION

Owing to strong economic incentives, processing of existing materials is becoming the best way to improve the properties of classical polymers and to generate new polymeric products. Blending is, of course, the least expensive and most versatile technique, although it is not always the most efficient. Good dispersions of polymer mixtures are easily achieved thanks to the powerful mixers and extruders now available; but the ultimate problem is to impart a satisfactory stability to these dispersions under processing conditions. Several procedures have been proposed to prevent phase segregation, by the crosslinking and the mechanical interlocking of components, or the development of interpenetrating networks¹. Nevertheless, the use of block polymers as stabilizing agents is recognized as a general and efficient means of controlling the morphology and mechanical behaviour of immiscible polymer blends^{2,3}.

Recent results obtained in our laboratory have illustrated the beneficial effects of polymeric emulsifiers in polymer mixtures⁴⁻⁸; indeed, the emulsification concept has been successfully applied to blends of polystyrene with low- or high-density polyethylene⁴⁻⁷. Similarly, the morphology and properties of polystyrene/poly(vinyl chloride) blends can be finely controlled⁸. These results have encouraged further extension of this technique to a wider range of polymers of basic technological and economic interest.

This report describes our investigations on poly(vinylidene fluoride)-based blends (PVF₂), a very attractive but expensive engineering polymer. It appears that, because poly(α -methylstyrene) (PMS) is an amorphous relatively cheap thermoplastic with a glass transition temperature (170°C) near the melting point of immiscible PVF₂ (168°C), appropriate PVF₂-PMS blends could result in commercial products with a balanced price-performance.

EXPERIMENTAL

The polymers used were PVF₂ Solef[®] 1012 ($\bar{M}_n = 80\,000$, $\bar{M}_w = 200\,000$) from Solvay and PMS ($\bar{M} = 85\,000$)

prepared in the laboratory by a classical anionic process (*s*-BuLi initiation in tetrahydrofuran at -78°C). The PMS-PMMA block copolymer was similarly synthesized by sequential anionic polymerization of α -methylstyrene and methyl methacrylate in tetrahydrofuran at -78°C with *s*-BuLi as initiator. Prepared in these experimental conditions, the PMMA block had a predominantly syndiotactic configuration (90%) and was accordingly miscible with PVF₂ (ref. 9). The block copolymer had a molecular weight of 180 000 and contained 50 wt% of each comonomer. Binary blends of PVF₂ with PMS, added with, respectively, 2 and 12 wt% of copolymer were prepared on a laboratory two-roll mill at 230°C for 5 min. The blends were then compression moulded at the same temperature for 5 min and at 2500 psi pressure and then allowed to cool to room temperature.

Tensile test specimens (DIN 53448) were prepared from compression-moulded sheets. Stress-strain measurements were made on an Instron tester at room temperature at a cross-head speed of 2 cm min⁻¹.

The morphology of the blends was investigated by both optical and scanning electron microscopy (s.e.m.). Microtomed sections (5 μ m thick) were observed by the optical technique after selective staining of the PMS phase according to a method devised in this laboratory¹⁰. Fracture surfaces prepared at liquid-nitrogen temperature were examined by s.e.m. (Philips 501-B).

RESULTS AND DISCUSSION

Evidence for the 'emulsifying' or 'compatibilizing' effect of poly(α -methylstyrene-*b*-methyl methacrylate) is clearly provided by the dramatic modifications induced in the morphology of the PVF₂/PMS blends (Figures 1 and 2). The unmodified blends exhibit large (ca. 50 μ m) domains of irregular size (Figures 1a and 2a). Very moderate amounts of the additive (2 wt%) greatly reduce and homogenize the particle size over the whole range of composition (Figures 1b and 2b). Rather finer dispersions (down to below 1 μ m) are obtained when a higher percentage of block copolymer (12%) is added (Figures 1c and 2c); however, that effect of a further increase in the additive percentage (from 2 up to 12%) on the decrease in particle size is relatively small.

* This report is the ninth paper in a series

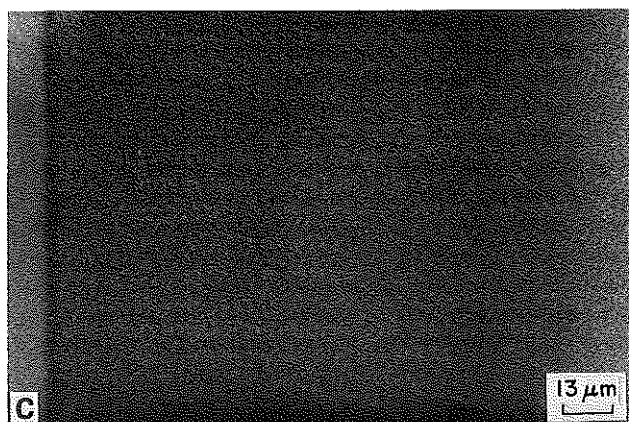
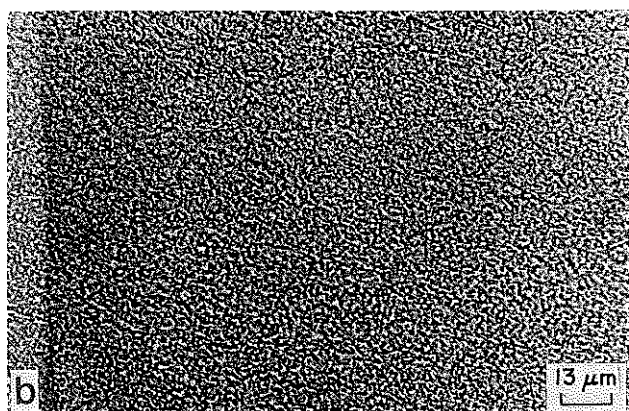
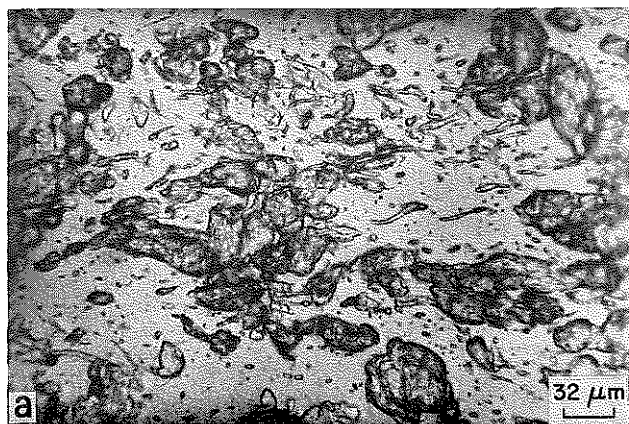


Figure 1 Optical micrographs of 80/20 PVF₂/PMS blends: (a) without block copolymer; (b) 2% block copolymer added; (c) 12% block copolymer added

The activity of the block copolymer is more obvious when the morphology of the blends is observed by using s.e.m. The unmodified blends exhibit a very coarse dispersion, characterized by the absence of interfacial adhesion (Figures 3a and 4a). The two-phase structure is dislocated by the cryofracture and the minor component is pulled out of its cavities, leaving holes with a very smooth surface. When 2% block copolymer is added, the morphology is modified considerably and the dispersed phase appears quite small, if observable at all (Figures 3b and 4b). Figure 3b shows that interfacial adhesion is sufficiently improved to prevent the breaking of 'threads' anchoring the phases together. When 12% block copolymer is used, the 'compatibilizing' effect is yet more pronounced (Figures 3c and 4c) and the blend containing 60% PVF₂ (Figure 4c) exhibits a surface fracture consisting of small (ca. 2000 Å) and regularly sized beads firmly bonded together.

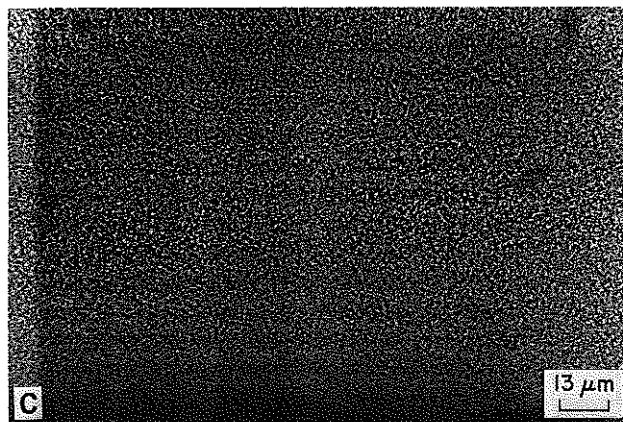
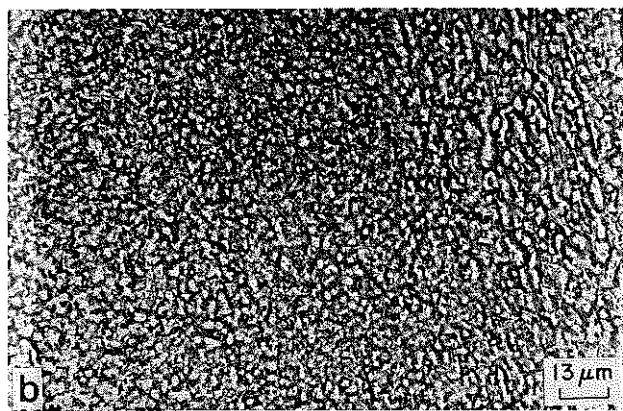


Figure 2 Optical micrographs of 60/40 PVF₂/PMS blends: (a) without block copolymer; (b) 2% block copolymer added; (c) 12% block copolymer added

The mechanical properties of pure PVF₂/PMS blends are rather poor, as demonstrated by their ultimate tensile strength (σ_B) and Young modulus (E) (Figures 5 and 6). These blends combine over a broad composition range the poorest properties of the components, i.e. low strength (σ_B) of PMS and low modulus of PVF₂. The addition of 2% block copolymer has a beneficial effect resulting in the approximate additivity of the modulus whatever the composition (Figure 6). A major effect is also observed on the mechanical strength (σ_B) of blends containing more than 40% PVF₂; σ_B is indeed higher than the value for pure PVF₂ in that composition range, and this synergism seems to be maximum at compositions of about 70% PVF₂ (Figure 5).

It is interesting to see that these improvements in σ_B and E are largely independent of the amount of block copolymer used, over the range 2–12%. The ductility (ϵ_B) of the pure blends is low and close to that for PMS, even

for PVF₂-rich blends (Table 1). It is rather disappointing to record no improvement of ductility in modified blends, whatever the amount of copolymer added.

CONCLUSIONS

From this preliminary evaluation of PVF₂/PMS blends, it can be concluded that poly(α -methylstyrene-*b*-methyl methacrylate) has an important 'bridging' (or

'compatibilizing') effect, as indicated by morphological investigations. When the block copolymer is added to the blends, a fine, regular and stable dispersion of phases is observed after melt blending and subsequent compression moulding. The fact that ductility stays so low (whatever the composition), whereas mechanical strength and modulus are significantly improved, remains an intriguing problem, in view of the good interfacial adhesion (illustrated by s.e.m.). Further investigations are

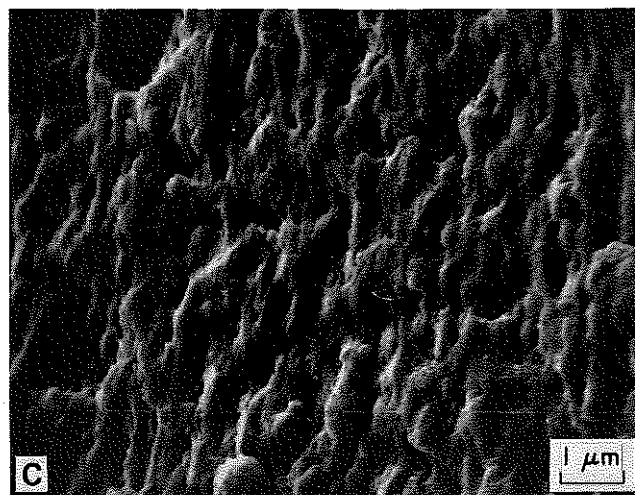
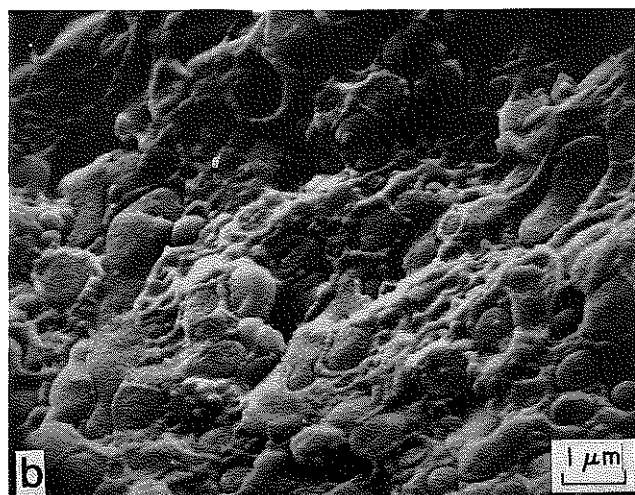
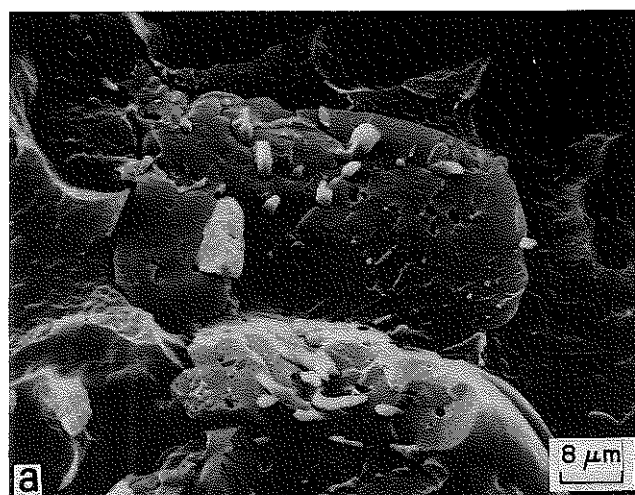


Figure 3 Scanning electron micrographs of 80/20 PVF₂/PMS blends: (a) without block copolymer; (b) 2% block copolymer added; (c) 12% block copolymer added

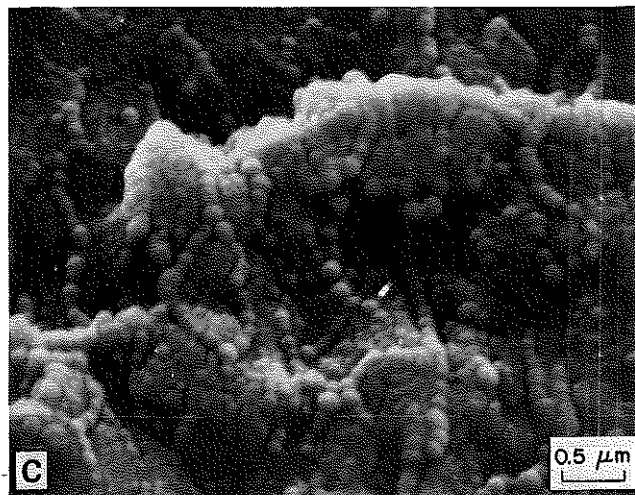
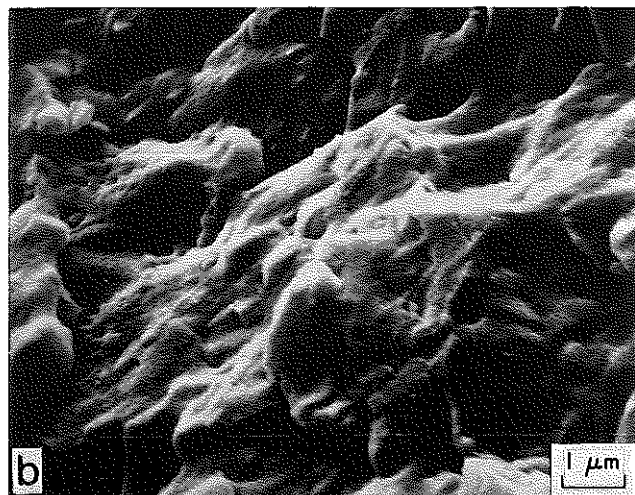
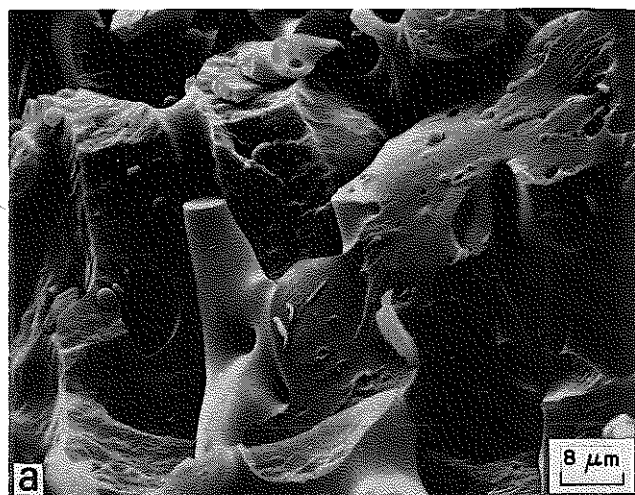


Figure 4 Scanning electron micrographs of 60/40 PVF₂/PMS blends: (a) without block copolymer; (b) 2% block copolymer added; (c) 12% block copolymer added

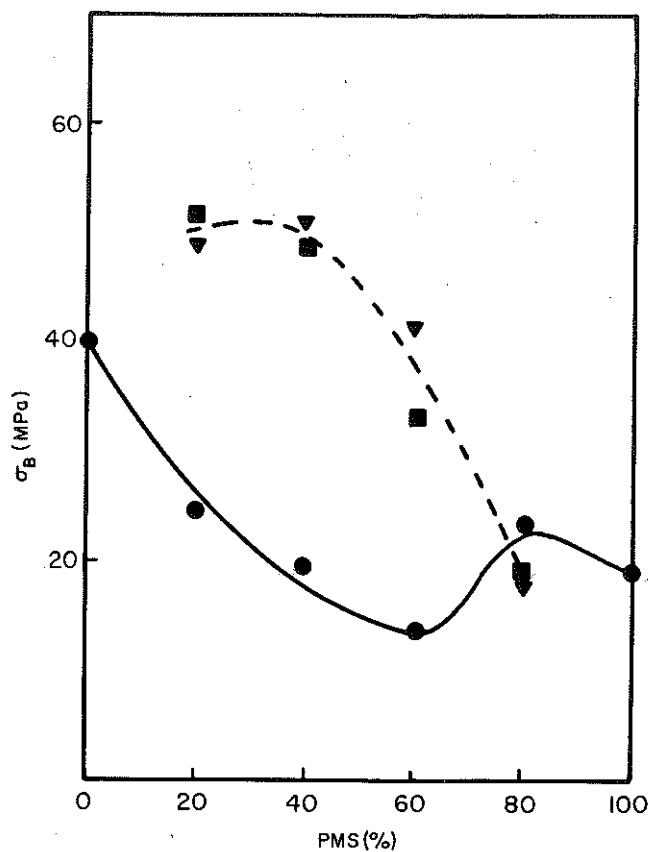


Figure 5 Ultimate tensile strength of PVF₂/PMS blends: ●, without block copolymer; ■, 2% block copolymer added; ▼, 12% block copolymer added

Table 1 Effect of the addition of block copolymer on the elongation at break of PVF₂/PMS blends

PVF ₂ (%)	PMS (%)	Block copolymer (%)	ε _B (%)
100	—	—	79
—	100	—	1
80	20	0	1–21
		2	3
		12	9
60	40	0	1
		2	<1
		12	<1
40	60	0	<1
		2	<1
		12	<1
20	80	0	<1
		2	<1
		12	<1

clearly necessary to better define the role played by the block copolymer, and also to improve the ductility of the PVF₂/PMS blends (possibly using a third rubbery phase).

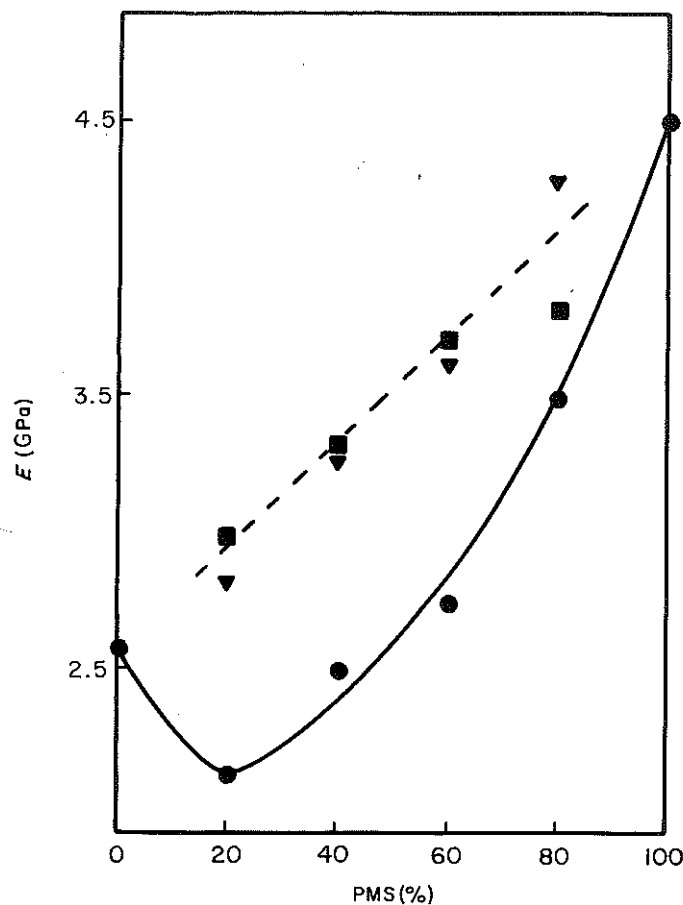


Figure 6 Young modulus of PVF₂/PMS blends: ●, without block copolymer; ■, 2% block copolymer added; ▼, 12% block copolymer added

ACKNOWLEDGEMENTS

The authors are indebted to IRSIA (Institut pour l'Encouragement de la Recherche dans l'Industrie et l'Agriculture) and to the Solvay Co. for efficient support. Y. Lambert is thanked for providing technical assistance.

REFERENCES

- 1 Thomas, D. A. and Sperling, L. H. in 'Polymer Blends' (Eds. D. R. Paul and S. Newman), Academic Press, New York, 1978, Vol. 2, Ch. 11
- 2 Paul, D. R. in 'Polymer Blends' (Eds. D. R. Paul and S. Newman), Academic Press, New York, 1978, Vol. 2, Ch. 12
- 3 Jerome, R. and Fayt, R. *Act. Chim.* 1980, September, 21
- 4 Fayt, R., Jerome, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Edn.* 1981, **19**, 79
- 5 Fayt, R., Jerome, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1269
- 6 Fayt, R., Jerome, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 2209
- 7 Fayt, R., Hadjiandreou, P. and Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 337
- 8 Fayt, R., Jerome, R. and Teyssié, Ph., to be published
- 9 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer-Polymer Miscibility', Academic Press, 1979, Ch. VI
- 10 Fayt, R., Palumbo, M. and Teyssié, Ph. LCMCO-2B Report (available from Ph. Teyssié on request under special agreement)