

Molecular Design of Multicomponent Polymer Systems. XVI. Emulsification of Polystyrene and Nylon-6 by a Reactive Block Copolymer

R. FAYT and PH. TEYSSIE, *Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman, B6, 4000 Liège, Belgium*

INTRODUCTION

One of the most attractive routes for alloying two incompatible polymers is the use of polymeric emulsifiers. The validity and applicability of this concept were widely demonstrated in the emulsification of polyethylene and polystyrene.¹⁻⁴

In its simplest form, the compatibilizer comprises blocks which are chemically identical to the respective components of the blend, although nonidentical segments which are miscible or partially miscible with the corresponding homopolymers should work equally well to promote a finer and more stable dispersion of the phases during mixing, and to improve interfacial adhesion and mechanical properties. The emulsification of blends based on poly(vinyl chloride), poly(vinylidene fluoride) or styrene-co-acrylonitrile resins by copolymers having a syndiotactic poly(methyl methacrylate) (PMMA) block illustrates fairly well the efficiency of this latter approach.⁵⁻⁸ A third approach for emulsification would exist in the use of a block which is not truly compatible with the homopolymer to be emulsified but which contains groups able to react with the latter, thus generating grafting during processing. For instance, a block bearing carboxylic acid groups is expected to undergo transamidation or transesterification reactions with polyamide or polyester chains; such a reaction was reported to take place during the melt processing of nylon-6 with polyolefins modified with maleic anhydride.⁹

In order to investigate the validity of this new concept of emulsification, we have examined the possibility of extending the use of block copolymers containing a syndiotactic PMMA block to the emulsification of polyamide-based blends by introducing carboxylic acid groups in the PMMA chains.¹⁰

This article aims at reporting preliminary results on the emulsification of polystyrene and nylon-6 blends by polystyrene-poly(methyl methacrylate-co-methacrylic acid) diblock copolymers, the carboxylic acid groups resulting from partial hydrolysis of methyl methacrylate units.

EXPERIMENTAL

Polystyrene-poly(methyl methacrylate) diblock copolymers, PS-PMMA of various molecular weights ($\bar{M}_n = 75,000$ to 220,000) and low polydispersity ($\bar{M}_w/\bar{M}_n = 1.1$) were synthesized by a well controlled anionic process using *s*-BuLi/ α -methylstyrene mixture as the initiator in THF at -78°C . Details of this procedure have been reported elsewhere.¹¹ Partial hydrolysis of PMMA chains (from 3% to 11%) was performed in refluxing acetic acid in the presence of para-toluene sulfonic acid for 3 to 7 days [3% and 8%-9% hydrolysis was obtained after 50 and 165 h, respectively, for a block copolymer having the following characteristics: 50 wt. % PMMA, \bar{M}_n (PMMA) =

70,000]. The homopolymers used for blending were a general purpose PS Polystyrol 158 K and a nylon-6 Ultramid B4, both from BASF.

PS/nylon 6 binary blends were prepared on a laboratory two-roll mill at 230°C for 5 min; they were then compression molded at 240°C for 3 min and allowed to cool to room temperature.

Blends with added block copolymers PS-PMMA or PS-P(MMA-co-MAA) were prepared under the same conditions. Generally, the copolymer was melt mixed with polyamide for 1 min before adding polystyrene and further mixing of the three components for an additional 4 min.

The morphology of the blends was examined by optical microscopy (5- μ m-thick microtomed sections) either under polarized light or by the phase contrast technique. Fracture surfaces prepared at room temperature were also examined by scanning electron microscopy (Philips 501-B).

DISCUSSION

Polystyrene and nylon-6 are recognized as being highly incompatible. The interfacial tension and rheological properties are therefore the main parameters which control the state of dispersion obtained by melt-blending the two polymers.¹² The observation of blends by optical and electron microscopy confirms that thermodynamic feature and its deleterious effects on morphology: coarsely dispersed phases of one polymer in the other are observed [Figs. 1(a) and 2(a)] and SEM of fracture surfaces shows, in addition, a complete lack of interfacial adhesion between the components [Fig. 2(a)]. Valuable additives for alleviating that situation were found in polystyrene-poly(ϵ -caprolactam) diblock copolymers.¹³ But the following results demonstrate unambiguously the high efficiency of more user-friendly PS-P(MMA-co-MAA) diblock copolymers in the control of the morphology of these incompatible blends.

Although PMMA and nylon-6 are not reported to be miscible, a reduction of the particle size is already observed upon addition of 5% PS-PMMA copolymer in PS/nylon-6 blends [Fig. 1(b)]. That situation might result from a decrease of the interfacial tension between PS and nylon-6, due to the presence of the block copolymer at the blend interface.¹² Moreover, partial grafting of nylon-6 on the PMMA block could also occur by exchange reactions during melt blending. This latter explanation is supported by the fact that only 70% of the PS-PMMA copolymer was extracted by THF (48 h at room temperature) after melt blending with nylon-6 (70 nylon/30 copolymer mixture). Nevertheless, a much more significant effect on the particle size is observed when the PMMA block contains a few percent (ca. 8%–10%) of methacrylic acid units [Fig. 1(c)]. Scanning electron micrographs of blends emulsified in this way also evidence a marked enhancement of the interfacial adhesion [Figs. 2(b) and (c)].

It is also shown that these block copolymers are very efficient in fairly small amounts: as little as 2% copolymer is sufficient to reduce the particle size of 50/50 PS/nylon-6 blend from 20–100 μ m to 1–5 μ m. Increasing the amount of copolymer up to 5% leads to a further particle size reduction to 0.5–1 μ m [Figs. 3(a) and (b)], which is not further decreased upon addition of 10% copolymer. Thus, 5% copolymer is sufficient to achieve an intimate mixing of PS and nylon-6. Furthermore this emulsifying efficiency is observed over a rather broad range of molecular weights (75,000 to 220,000) and composition (90% to 50% PS), at least when the particle size is considered [Figs. 4(a) and (b)].

As to the amount of carboxylic acid in the PMMA chain, Fig. 5(a) shows that 3% hydrolysis of a PS-PMMA copolymer ($\bar{M}_n = 140,000$, 50% PS, 22 COOH units per PMMA chain) is sufficient to obtain a finely dispersed PS/nylon-6 mixture with a particle size of about 1–3 μ m. When the COOH content of the same copolymer is

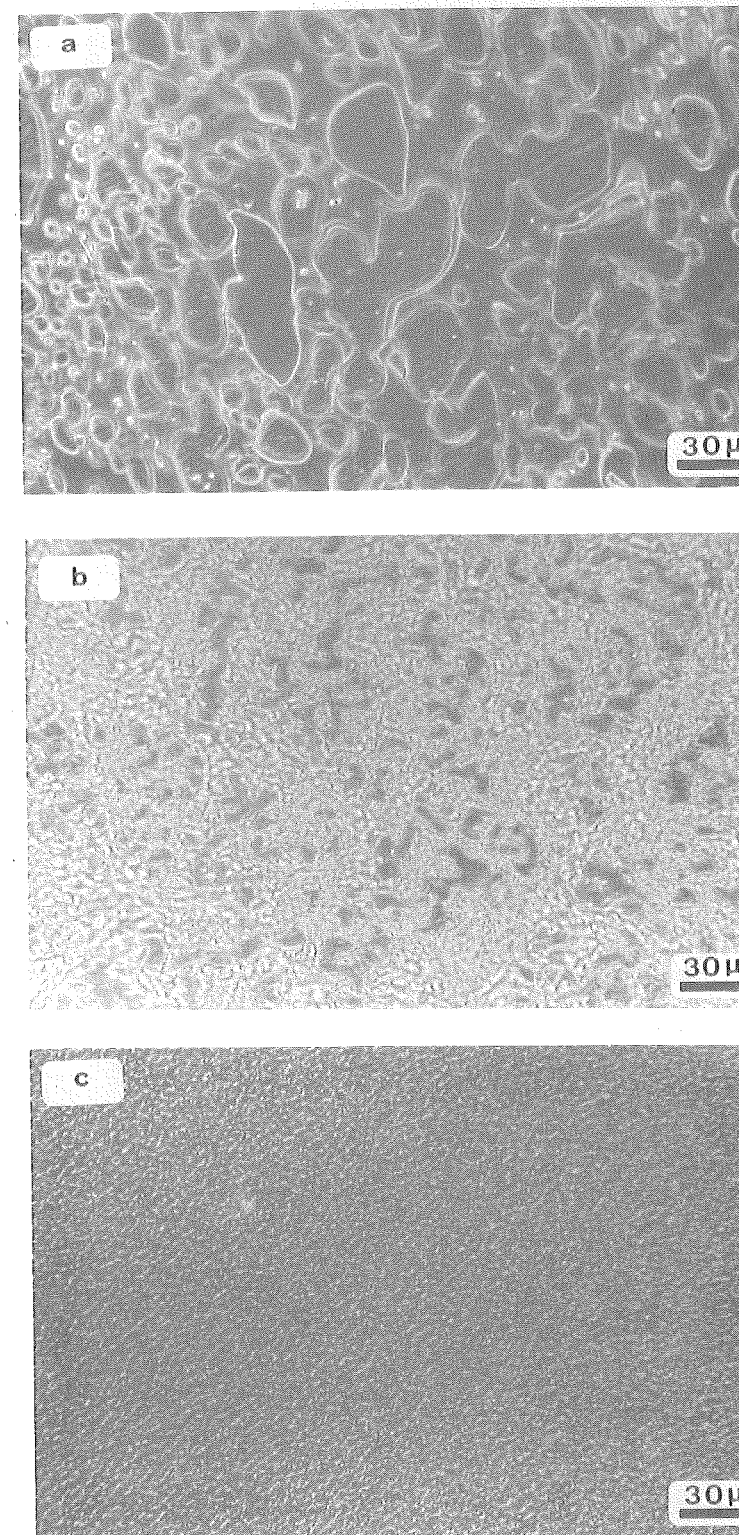


Fig. 1. Phase contrast micrographs of 50 PS/50 nylon-6, (a) no copolymer, (b) with 5% PS-PMMA ($\bar{M}_n = 200,000$, 90% PS), and (c) with 5% PS-P(MMA-co-MAA) ($\bar{M}_n = 200,000$, 90% PS, 10% MAA in PMMA).

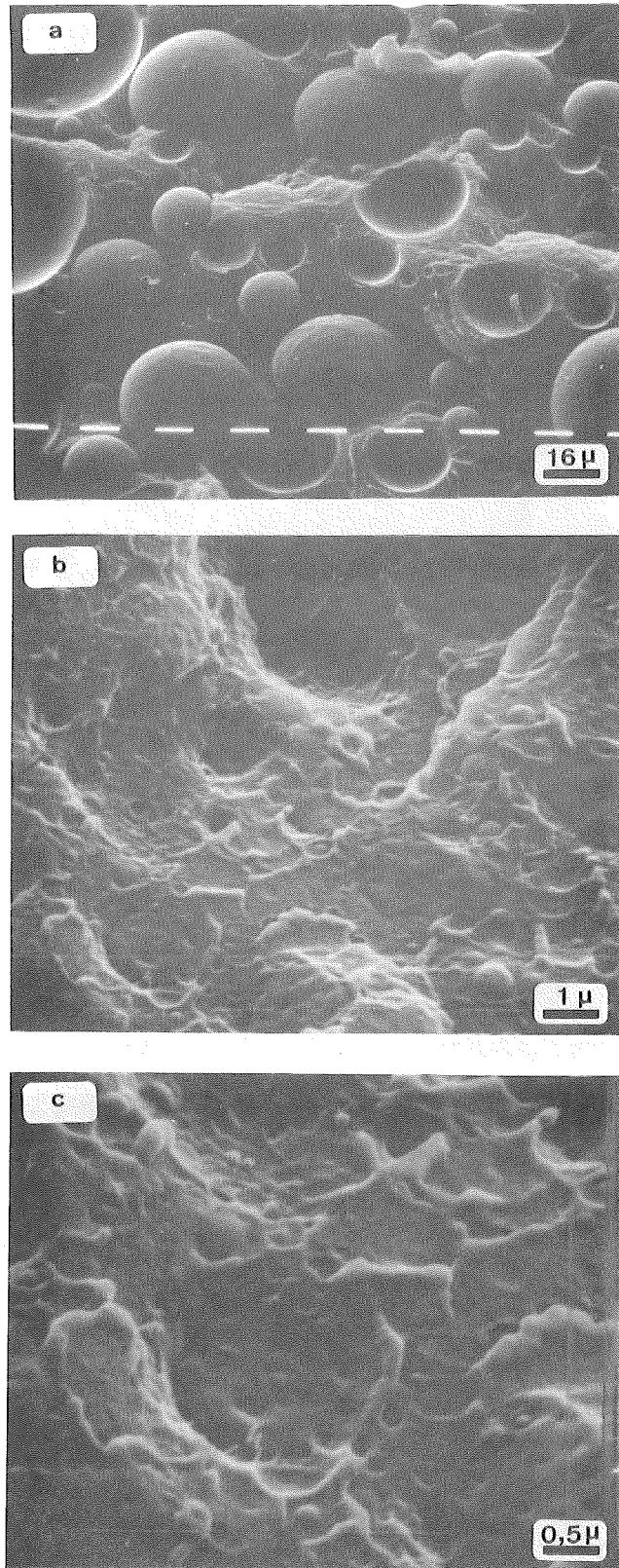


Fig. 2. Scanning electron micrographs of 50 PS/50 nylon-6 (fracture surfaces at room temperature) (a) no copolymer, (b) with 5% PS-P(MMA-co-MAA), ($\bar{M}_n = 220,000$, 50% PS, 8% MAA in PMMA), and (c) detail of (b).

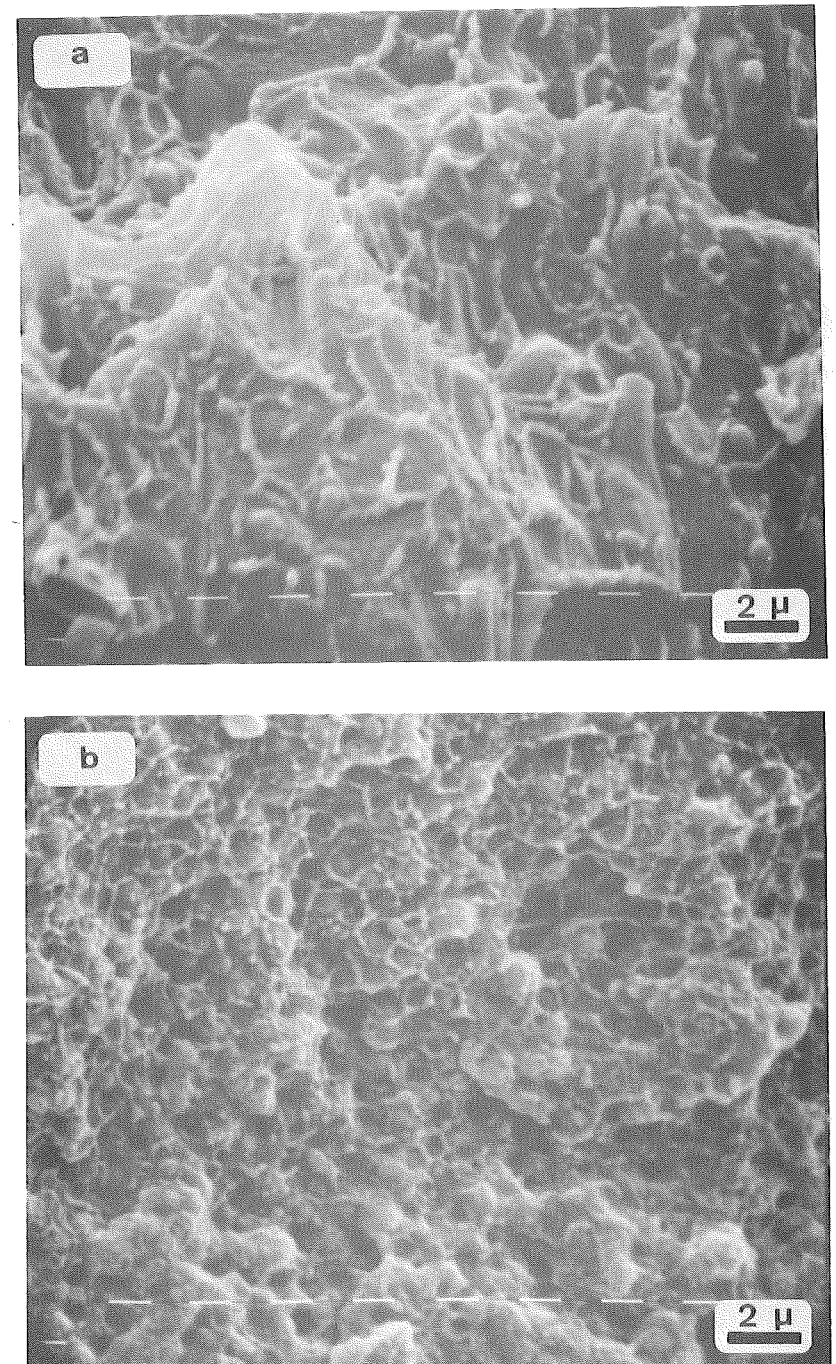


Fig. 3. Scanning electron micrographs of 50 PS/50 nylon-6 (fracture surfaces at room temperature) (a) with 2% PS-P(MMA-co-MAA) ($\bar{M}_n = 100,000$, 50% PS, 9% MAA in PMMA), and (b) with 5% of the same.

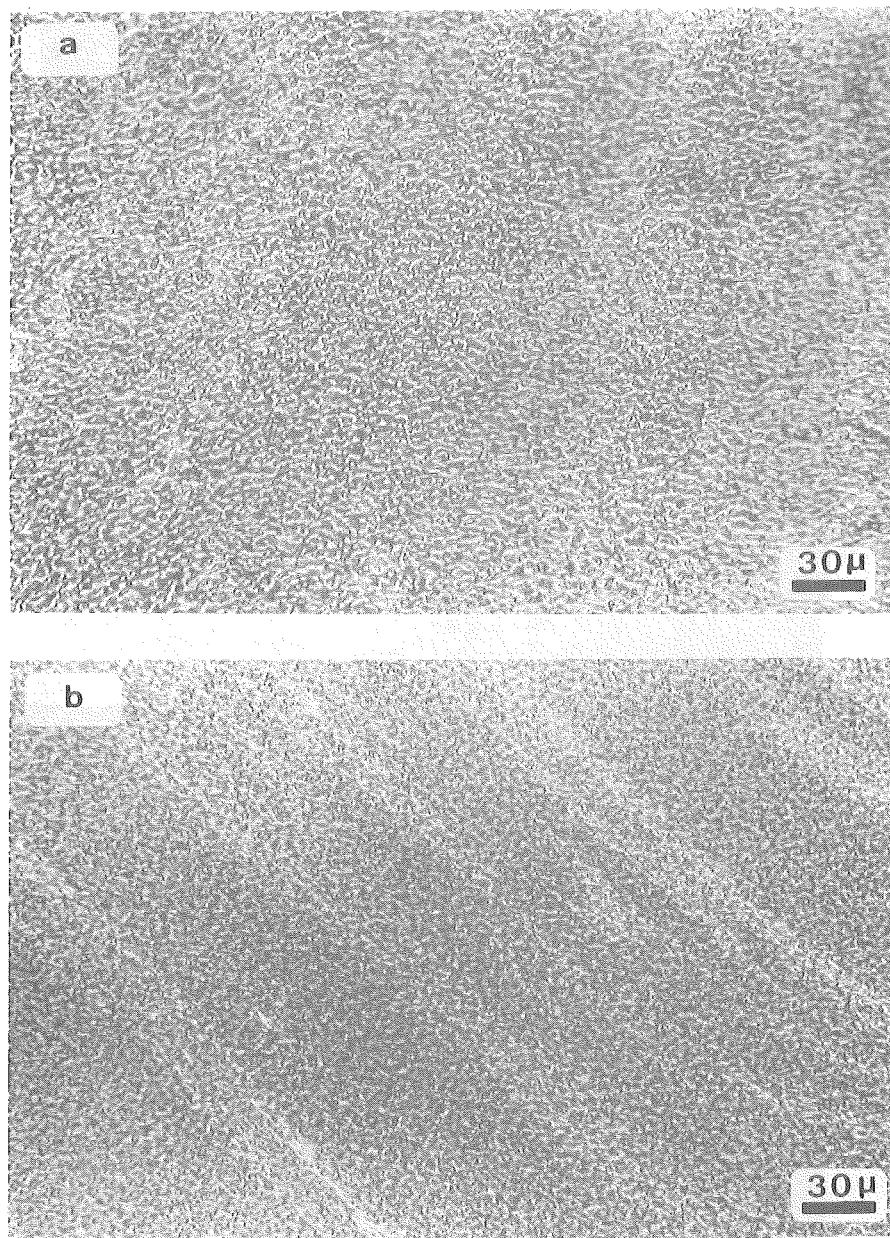


Fig. 4. Phase contrast micrographs of 50 PS/50 nylon-6 with added 5% PS-P(MMA-co-MAA) (50% PS, 9% MAA in PMMA) (a) $\bar{M}_n = 75,000$, and (b) $\bar{M}_n = 140,000$.

increased up to 8%–10% (60–70 COOH units per chain), the particle size of the blend is further decreased to 0.5–1 μm [Fig. 5(b)].

Deeper insight into the morphology together with the evaluation of the mechanical behavior of PS/nylon-6 blends as modified by these block copolymers is needed to ascertain the optimum values for molecular characteristics and acid content of these emulsifiers.

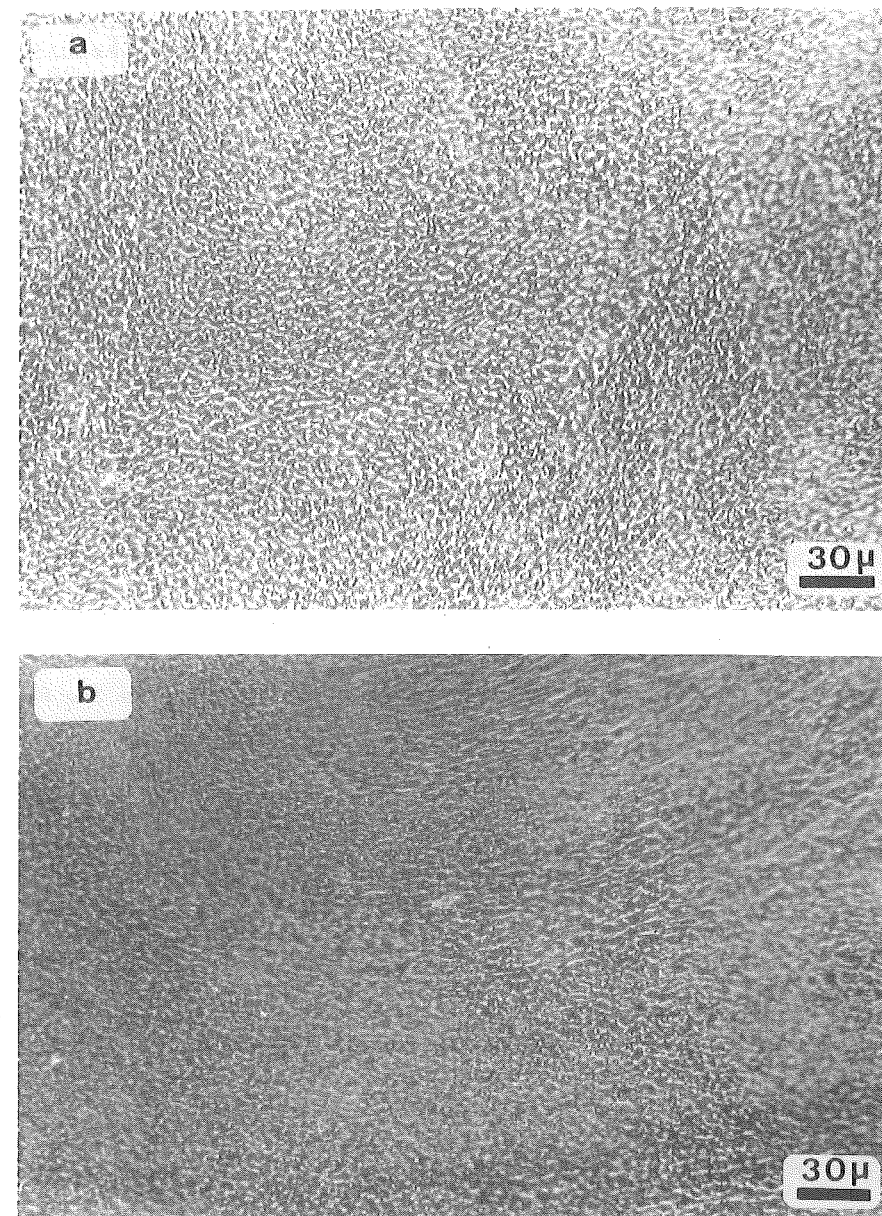


Fig. 5. Phase contrast micrographs of 50 PS/50 nylon-6 with added 5% PS-P(MMA-co-MAA) ($\bar{M}_n = 140,000$, 50% PS) (a) 3% MAA and (b) 8.5% MAA in PMMA.

Nevertheless, the actual results demonstrate unambiguously the efficiency of hydrolyzed PMMA blocks in the emulsification of PS/nylon-6 blends. The fact that most of the copolymer cannot be solvent-extracted after melt blending with nylon-6 is an indication that grafting occurs to a significant extent between PS-P(MMA-co-MAA) and nylon-6 during melt mixing. In a significant experiment, a 70% nylon-6/30% PS-P(MMA-co-MAA) mixture (\bar{M}_n copolymer = 140,000, 50% PS, 9.5% MAA on PMMA block) was THF-extracted for 48 h at room temperature: only 2% of the

initial amount of copolymer was recovered (compared to results reported above for the corresponding nylon-6/PS-PMMA mixture: 70% copolymer extracted under the same conditions).

More systematic and quantitative investigations are now envisioned in order to gain precise information on the degree of grafting in relation with the molecular characteristics of block copolymers, carboxylic acid content, and melt blending conditions. An obvious direct extension of these results may also be sought in the emulsification of nylon-6 (or 6.6)/polyethylene blends, using a poly(hydrogenated butadiene-*b*-MMA-co-MAA) additive.

In conclusion, these preliminary results give a very optimistic forecast for this emulsification approach which could be of general applicability for incompatible blends based on polycondensates able to undergo exchange reactions (an important part of engineering plastics).

The authors are indebted to ISOVER St Gobain who sponsored this research and to SPSS (Services de la Programmation de la Politique Scientifique) for continuous financial support. We also want to thank M. Palumbo for skillful technical assistance, particularly in morphology investigations.

References

1. D. R. Paul in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, Vol. 2, Chap. 12.
2. C. G. Locke and D. R. Paul, *J. Appl. Polym. Sci.*, **13**, 2597 (1973).
3. D. Heikens, N. Hoen, W. M. Barensten, P. Piet, and H. Ladan, *J. Polym. Sci., Polym. Symp.*, **62**, 309 (1978).
4. R. Fayt, R. Jérôme, and Ph. Teyssié, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 79 (1981); *ibid. J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1269 (1981); *ibid. J. Polym. Sci., Polym. Phys. Ed.*, **20**, 2209 (1982); *ibid. Makromol. Chem.*, **187**, 837 (1986); *ibid. J. Polym. Sci., Polym. Phys. Ed.*, **27**, 775 (1989).
5. R. Fayt and Ph. Teyssié, *Macromolecules*, **19**, 2077 (1986).
6. T. Ouhadi, R. Fayt, R. Jérôme, and Ph. Teyssié, *Polym. Comm.*, **27**, 212 (1986); *ibid. J. Polym. Sci., Polym. Phys. Ed.*, **24**, 973 (1986); *ibid. J. Appl. Polym. Sci.*, **32**, 5647 (1986).
7. Ph. Teyssié, R. Fayt, and R. Jérôme, *Makromol. Chem. Symp.*, **16**, 41 (1988).
8. R. Fayt, R. Jérôme, and Ph. Teyssié, *Polym. Eng. Sci.*, **27**, 328 (1987).
9. F. Ide and A. Hasegawa, *J. Appl. Polym. Sci.*, **18**, 963 (1974).
10. R. Fayt, Ph. Teyssié, and D. Hanton, French Patent 2,582,659, July, 1987.
11. Ph. Teyssié, R. Fayt, R. Jérôme, and T. Ouhadi, U.S. Patent 4,461,874, July 24, 1984.
12. S. Wu, *Polym. Eng. Sci.*, **27**, 335 (1987).
13. D. Petit, R. Jérôme, and Ph. Teyssié, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2905 (1979).

Received July 12, 1988

Accepted May 8, 1989

Preparation of Polymer Crystal Nuclei

NI DING and ERIC J. AMIS,* *Department of Chemistry, University of Southern California, Los Angeles, California 90089*, RONALD SALOVEY, *Department of Chemical Engineering, University of Southern California, Los Angeles, California 90089*, and ROBERT M. BRIBER, *Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

An alternative method has been developed to prepare suspensions of polymer crystals. The crystals are formed by rapidly freezing a clean toluene solution of poly(ethylene oxide) to low temperature. When the frozen solution is warmed to room temperature, it provides a suspension of uniform and stable particles. These particles have been used as seeds for nucleating solution-grown PEO crystals. The diameters of the seeds are measured by dynamic light scattering to be 0.16–0.8 μm for solutions with concentrations ranging from 5 to 400 $\mu\text{g/g}$. Transmission electron micrographs show the seeds to be clusters of square PEO lamellae. A possible mechanism for the seed formation is discussed.

INTRODUCTION

During dynamic light scattering investigations of the kinetics of polymer crystallization from dilute solution,¹ a new method has been developed to prepare polymer crystal nuclei. This article discusses some of these observations, specifying as an example the behavior of solutions of poly(ethylene oxide) in toluene.

Two methods have been previously reported to prepare seeds from solution—the self-seeding method² and the droplet method.^{3,4} In the first method, a polymer solution is brought to a crystallization temperature, T_{c1} . After the polymer has crystallized, the suspension is immersed in a thermal bath, $T_s (> T_{c1})$, to partially dissolve the crystals and leave suspended uniform seeds. For kinetic measurements, the suspension is cooled to a desired crystallization temperature, T_{c2} , where dissolved polymer in the solution will deposit on the seeds. The primary nuclei of these crystals are thought to be largely heterogeneous. Since it was first developed in 1966, self-seeding has been widely used for studies of the kinetics of solution-grown crystals with a variety of techniques, which included optical and electron microscopy⁵ as well as small angle static light scattering (SALS).^{6,7} In a clever SALS method for solutions, an electric field is applied across a dilute solution to orient the crystals and the scattering of vertically, and horizontally polarized incident light is analyzed based on a special model function. The dependency on a model function limits this method.

For seed preparation by the droplet method, xylene and nitrobenzene solvents are initially purified and filtered (0.2 μm pore filter). Small quantities of hot, concentrated, polyethylene-xylene solution are poured into boiling nitrobenzene, whereupon most of the xylene immediately boils away. The PE-nitrobenzene solution is cooled to room temperature, producing a dispersion of frozen PE droplets which are separated from

*To whom all correspondence should be addressed.