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Two-step etching procedures for binary polymer blends

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Two-step etching procedures have been developed for binary polymer blends of linear low density polyethylene (LLDPE) with high density polyethylene (HDPE), and for blends of atactic and syndiotactic polystyrene. For both cases, two different etchants have been identified for the component neat polymers; sequential etching has been employed to reveal the distribution of the component polymers within the blend. It is believed that similar procedures may be applicable to other blend systems. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyethylene; etching; polystyrene)

INTRODUCTION

In the 1970s, D. C. Bassett *et al.* introduced a technique for etching polyethylene with a permanganic reagent[1–3]. The etchant, a strong oxidizer, attacks the surface[2], areas of crystal disorder[2], amorphous regions[4], and damaged regions[5]; the oxidized material is removed, leaving the lamellar crystallites intact. The use of such etchants in conjunction with electron microscopy is now widespread, and the microstructures of a variety of polymers have been revealed using this technique; these polymers include various polyolefins[6], poly(aryl ether ether ketone)[7], and poly(aryl ether ketone ketone)[8], among others.

In the present study, the morphologies of blends of linear low density polyethylene, LLDPE, with high density polyethylene, HDPE, are of interest, as are blends of atactic and syndiotactic polystyrene. In both cases, it has been observed that the optimal etchant for the component neat polymers are different. This has led to speculation that sequential exposure to the two etchants could lead to new information concerning the distribution of the component polymers within the blends.

EXPERIMENTAL PROCEDURES

HDPE/LLDPE blends

Three neat polymers have been used in this study: a linear low density polyethylene copolymer (LLDPE), Exxon Exact 3025, and two narrow fractions of high density polyethylene, (HDPE). The physical properties of the polymers are given in *Table 1*. One-to-one blends, by weight, of the linear low density and the high density polyethylenes have been prepared by dissolving the two components in boiling xylene and then precipitating rapidly into methanol[9,10]; the blends are designated as 27.7 K 50/50 and 41.7 K 50/50, indicating the molecular weight of the HDPE component within the 50/50 blend. In all cases, precipitation appears to have been instantaneous and homogeneous. The solvents have been evaporated from the precipitate by heating under vacuum at 80–85°C for at least 24 hours. Isothermal crystallization of samples with a thickness of 0.76 mm has been performed in a Mettler FP82 hot stage at the desired crystallization temperature[9]. Samples used in this work have been crystallized at 105 ± 1.06°C, for approximately 30 min.

Attempts to etch the pure LLDPE copolymer have shown that a variation of the etchant recipe proposed for poly(aryl ether ketone ketone)[8] is optimal in revealing the lamellar-level microstructure[9]; the exact chemical formula and etching times are given in *Table 2*. A variation of the recipe introduced by Bassett and colleagues for HDPE has been successfully used to etch the two HDPE homopolymers; the exact formula and times are given in *Table 2*.

Since the HDPEs and LLDPE are optimally etched in different chemical formulations, a sequential etching process has been proposed which would identify the locations of the two component polymers within the blend[11]. The sample is first etched in the LLDPE etchant, the weaker of the two etchants, for half an hour, as per the standard etching of LLDPE. One half of the sample is saved for examination, while the remainder is etched via a 10 min exposure to the standard HDPE etchant. The procedure is also summarized in *Table 2*.

The etched samples have been used in a variety of microscopic techniques. The etched surface has been used in atomic force microscopy, AFM, and for preparing two-stage, Pt-C replicas for use in the transmission electron microscope, TEM[9]. Samples have also been prepared for viewing in the SEM by sputter-coating a thin layer of gold on the surface[9].

Polystyrene blends

Atactic and syndiotactic polystyrene homopolymers, a-PS and s-PS, respectively, have also been blended together; the properties of the two component polymers are given in *Table 3*. Blends of atactic and syndiotactic polystyrene have been prepared by dissolving the components in 1,2-dichlorobenzene, and then precipitating into

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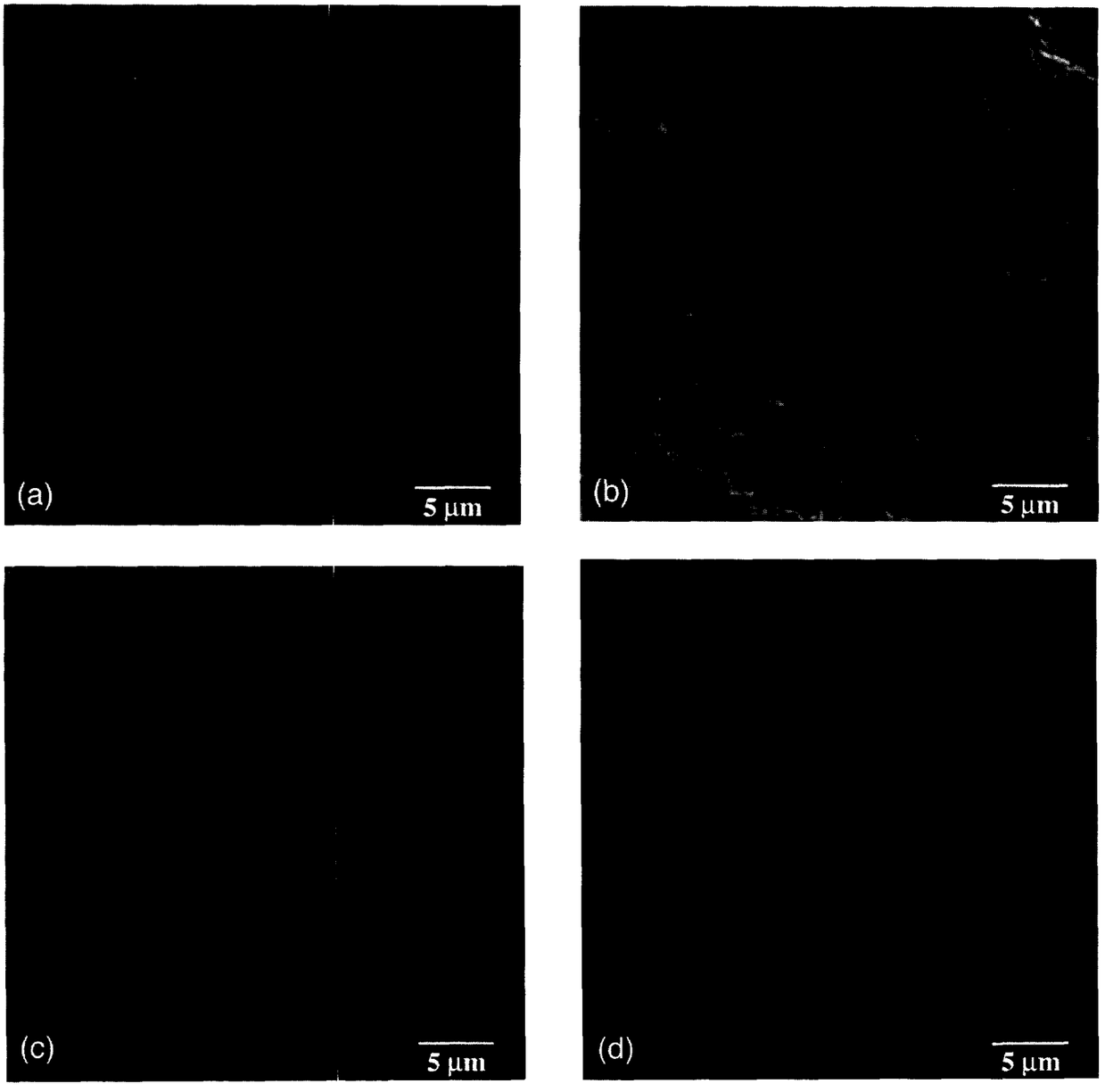

Figure 1 Sequential etching of LLDPE/27.7 K HDPE sandwich: (a) LLDPE side after first etch; (b) HDPE side after first etch; (c) LLDPE side after second etch; (d) HDPE side after second etch. All are SEM images of etched, sputtered surfaces

Table 1 Physical properties of neat LLDPE and HDPE polymers

Property	LLDPE	27.7 K HDPE	41.7 K HDPE
M_w (elution volume)	59 826	27 700	41 700
M_w/M_n	2.04	1.99	3.66
Branching	21/1000 C	< 1/1000 C	< 1/1000 C

methanol. Precipitation appears to have been homogeneous. The solvents have been evaporated from the precipitate at ambient conditions for 2 days and then under vacuum at 120°C for at least 40 hours[12]. Isothermal crystallization of thin samples with a thickness of approximately 0.10 mm has been performed in a hot stage at the desired crystallization temperature[12]. Samples used in this work have been crystallized at 250 ± 1°C[12].

The blends have been etched for 30 s in amyl acetate, a solvent for the amorphous polystyrene[12]. A portion of the sample has been saved for microscopic examination. The remainder has then been etched for 2 hours in a solution of 1 wt% $KMnO_4$ in sulfuric acid. The etched samples have been prepared for SEM, AFM, and TEM analysis using the same methods described above for the LLDPE/HDPE blends.

RESULTS AND DISCUSSION

HDPE/LLDPE blends

The validity of this two-step process in revealing different aspects of the microstructure has been confirmed by processing an HDPE/LLDPE sandwich. Small portions of the two neat polymers have been melted, side-by-side, and

Table 2 Etching conditions for LLDPE/HDPE blends

Polymer		Weight % $KMnO_4$	Volume % H_3PO_4	Volume % H_2SO_4	Volume % H_2O	Duration (min)
LLDPE		2.0	33.50	55.75	11.00	30
27.7 K HDPE		3.5	50	50	0	30
41.7 K HDPE		3.5	50	50	0	30
Blends	(1)	2.0	33.50	55.75	11.00	30
(2-step)	(2)	3.5	50	50	0	10

Table 3 Physical properties of neat atactic and syndiotactic polystyrene polymers

Property	Atactic PS	Syndiotactic PS
M_w	498 000	500 000
M_w/M_n	1.2	2.1

then crystallized. The resulting sandwich has been processed, and has been examined after each etching step: *Figure 1a* and *b* show the LLDPE and HDPE sides, respectively, following the first step; *Figure 1c* and *d* show the two sides following the second etch. Following the first etch, the banded spherulite structure of the LLDPE is revealed very nicely, but the HDPE half is underetched[9,11]. After the second etch, the LLDPE is severely overetched, while the axialitic HDPE structure is revealed very clearly[9,11]. This test indicates that if the two component polymers are segregated into discreet areas within the blend, a single etching step will not be sufficient to identify both. There is no indication in the literature that such a two-step process has been used for polyethylene blends.

The 27.7 K 50/50 blend has been etched using the two-step procedure. *Figure 2a* and *b* show SEM images of a 27.7 K 50/50 blend, crystallized at 105°C, following the first and second etching steps, respectively. Bands are clearly evident after the first etch, but there is little definition of structure within the bands, or in the centre of the spherulite. Following the second etch, an axialite is clearly shown in the centre of the banded spherulite, and the bands are much more detailed.

There are many pits evident in the two images, which are revealed more clearly using AFM; using three-dimensional AFM images, it is evident that these pits deepen following the second etch, as shown in *Figure 3a* and *b*. The two images are scaled to the same dimensions in all three directions. Comparing the three-dimensional images of the structure revealed by the two etching steps is very helpful. It is very evident that, after the first etch, neither the spherulites, nor the bands which are revealed, are deeply etched. The pits are also relatively shallow, and are moderate in diameter. Following the second etch, the spherulites and bands are much more deeply etched. The pits are substantially deeper and broader. There are also deep groves between the lamellae in the bands; this is consistent with Bassett's observations[13] for HDPE.

Here, it is suggested that during the first etching step, primarily the LLDPE components are etched, and amorphous LLDPE is removed. The pits which are revealed tend to lie between spherulites, and so are assumed to have been filled with small pockets of amorphous LLDPE; the existence of such pockets of unincorporated LLDPE has been confirmed by differential scanning calorimetry[9]. During the second etch, it has been demonstrated that

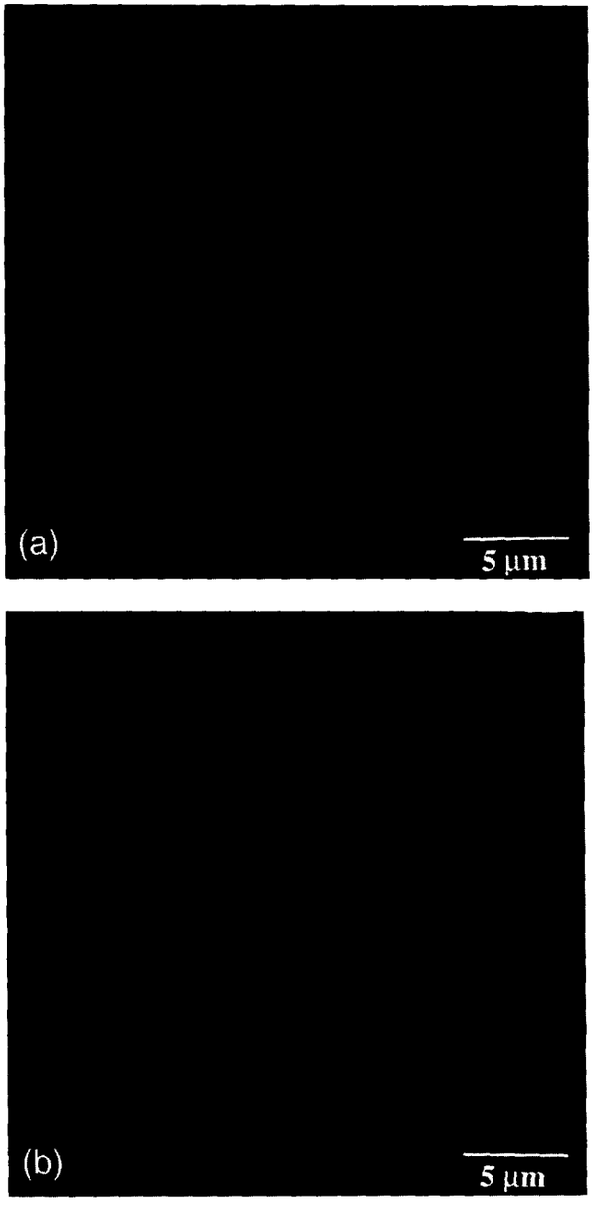

Figure 2 27.7 K 50/50 blend, T_c = 105°C: (a) after first etch; (b) after second etch. SEM images of etched, sputtered surface

crystalline LLDPE is removed; amorphous HDPE is also removed. The deep pits are believed to have been pockets of LLDPE which were trapped between the spherulites. The overall spherulitic structure is more deeply revealed during the second etch, suggesting an HDPE-like composition;

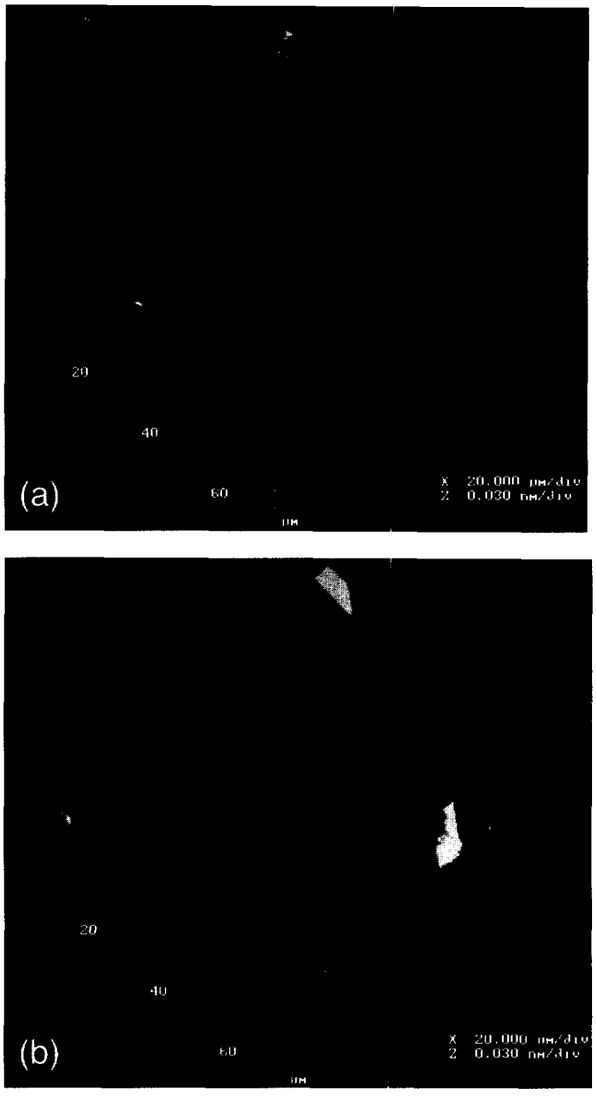

Figure 3 27.7 K 50/50 blend, T_c = 105°C: (a) after first etch; (b) after second etch. Three-dimensional AFM images of etched surface

Figure 4 27.7 K 50/50 blend, T_c = 105°C, after *n*-heptane etch. AFM image of etched surface, amplitude mode. This shows the gradients in topography of the image, thus enhancing the image of the inter-spherulite areas of interest

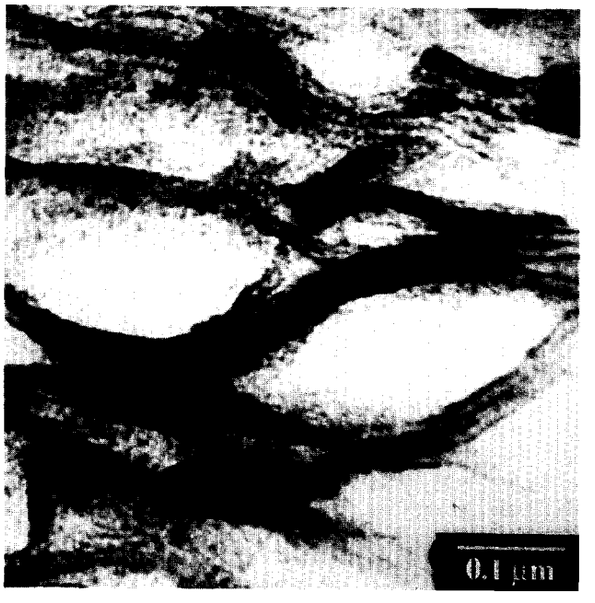

Figure 5 Lamellar structure of 27.7 K 50/50 blend, T_c = 105°C. Sample has been sequentially etched in *n*-heptane, and two potassium permanganate-based etches. Two-stage Pt-C TEM replica

d.s.c. studies indicate that the superstructure is composed of co-crystals of the HDPE and LLDPE[9].

To confirm that LLDPE is indeed being removed from the interspherulitic regions, an identical sample has been prepared. However, instead of etching in the potassium permanganate solutions, this sample has been etched for 20 min in *n*-heptane, at 60°C, as suggested by Mirabella[14]. It has been shown that *n*-heptane is a solvent for LLDPE; however, HDPE samples exposed to the same conditions have been largely unaffected by the *n*-heptane. Therefore, it can be assumed that only LLDPE will be removed during the *n*-heptane exposure. When examined in the AFM, boundaries between the spherulites are very evident; however, they are not seen in the permanganate-etched samples. This supports the suggestion that pockets of LLDPE have been removed from the areas between the spherulites. The spherulite boundaries are shown in *Figure 4*. Part of this heptane-etched sample has also been sequentially etched. The final microstructure is indistinguishable from that of the permanganate-etched samples, so it can be assumed that the *n*-heptane has affected only the LLDPE that is segregated out of the spherulites. A lamellar-level micrograph of the blend is shown in *Figure 5*.

A similar set of experiments have been performed on the 41.7 K 50/50 blend, also crystallized at 105°C. In this case, both the 41.7 K homopolymer and the LLDPE copolymer form banded spherulites, as does their blend. As with the 27.7 K blend, more details of the structure are revealed following the second etching step, indicating an HDPE-like structure. Large pits of unincorporated LLDPE are also

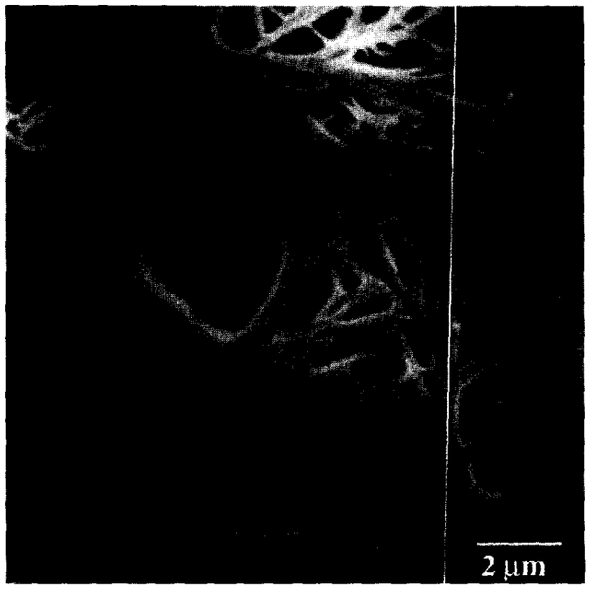

Figure 6 Bundles of s-PS in a-PS/s-PS blend. SEM image, amyl acetate etched sample

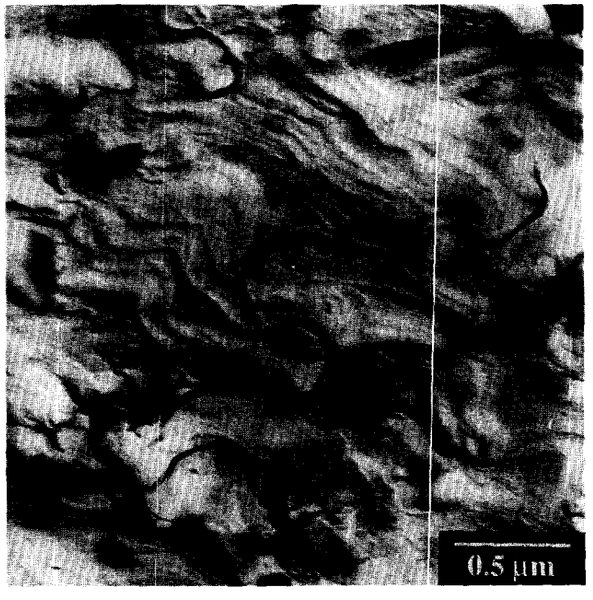

Figure 7 Lamellar level structures of s-PS in a-PS/s-PS blend. TEM image, doubly etched sample, two-stage replica

revealed, as with the other blend. Again, d.s.c. studies suggest that the blend is composed of co-crystals of the HDPE and LLDPE, and that some LLDPE is excluded from the crystals[9].

Polystyrene blends

Following exposure to the amyl acetate, bundle-like structures are revealed in the blend, as shown in *Figure 6*. It is known that the atactic polymer does not crystallize; therefore, it can be assumed that the bundles are composed of lamellae of the s-PS[10]. In order to reveal the lamellar-level structure within the bundles, it is necessary to etch the samples in the potassium permanganate solution. This etching step removes the interlamellar material. The lamellae are shown in *Figure 7*.

CONCLUSIONS

It is evident that sequential etching of polymeric blends can be used to reveal different aspects of the polymer morphology. For blends of LLDPE with HDPE, a two-step etching process has been developed in which the potassium permanganate-based etchants for the two component polymers are used to reveal the locations of unincorporated LLDPE and the superstructures of the crystalline material. For blends of atactic and syndiotactic polystyrene, the two-step etching procedures uses a solvent for the amorphous, atactic material to reveal the bundle structure of the crystallized s-PS, and a potassium permanganate-based etchant to reveal the lamellar-level structure within those bundles.

It is believed that similar sequential etching procedures can be developed for other polymer blends which would help in the microscopic examination of the morphologies.

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