

# Selective Etching of Thermotropic Liquid Crystalline Polyesters

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## Synopsis

DSC, IR, ESCA, macroscopic etching rate measurements, analysis of etchant solution, and electron microscopy conclusively show that *n*-alkylamines (ethylamine, *n*-propylamine, *n*-butylamine, and *n*-pentylamine) and NaOH selectively degrade (etch) the ethylene terephthalate (ET)-rich phase in glassy liquid crystalline poly(*p*-hydroxybenzoic acid-co-ethylene terephthalate) [P(HBA-ET)] with molar compositions 0.60:0.40 and 0.80:0.20. ESCA demonstrates the excellent selectivity of the *n*-alkylamine etchants in the 0.60:0.40 copolymer. The 50 Å top layer of the etched samples contains 95 mol% HBA. Treatment with H<sub>2</sub>SO<sub>4</sub> and NH<sub>3</sub> gives ambiguous results, and these compounds are not suitable as etchants. It is demonstrated by electron microscopy on the 0.60:0.40 copolymer, in accordance with earlier reports by Joseph et al.,<sup>5-8</sup> that the ET-rich phase is discontinuous (1-2 μm spheres) and surrounded by an HBA-rich matrix. SEM is a useful tool for characterization of this morphology. However, both phases have a substructure which is revealed only by TEM. The morphology of the 0.80:0.20 copolymer is fine-textured, which means that SEM is a less suitable method for the characterization of etched samples.

## INTRODUCTION

Thermotropic liquid-crystalline copolyesters are a relatively new group of high performance polymers. One of the first copolyesters, based on *p*-hydroxybenzoic acid (HBA) and ethylene terephthalate (ET), was synthesized by Jackson et al.<sup>1-3</sup> and has been the subject of a number of papers.<sup>1-17</sup> In the present paper results are presented from the etching of two representatives of these copolyesters: P(HBA-ET) with molar ratios 0.60:0.40 and 0.80:0.20.

Jackson and Kuhfuss<sup>1</sup> have presented NMR and WAXS data in favor of a random distribution of the comonomer units in the P(HBA-ET) 0.60:0.40 polymer. The occurrence of two glass transitions in this polymer, however, provides clear evidence for the existence of separate phases rich in HBA and ET, respectively.<sup>10</sup>

Joseph et al.<sup>4-8</sup> present data from electron microscopy and ESCA in favor of the heterogeneity of the 0.60:0.40 copolymer and the existence of ET- and HBA-rich domains of micron size.

The molecular structure and morphology of P(HBA-ET) 0.80:0.20 is less disputed. Zachariades et al.<sup>16,17</sup> have shown that the structure of the copolyester is not random, but that the material is composed of blocks of the two comonomers. These authors<sup>16,17</sup> have also found some evidence for the existence of a minor amount of homopolymer of PHBA in the P(HBA-ET)

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copolymer. Transmission electron microscopy, electron diffraction, and X-ray analysis provide evidence that the P(HBA-ET) 0.80 : 0.20 copolymer consists of long sequences of HBA in discrete domains with a well-defined lamellar structure with a lamellar thickness of 200–400 Å.<sup>16,17</sup>

Etching is a widely used method of studying morphology in multicomponent polymers. Etching involves the selective removal of one or several of the components from the samples. This treatment is normally followed by an examination of the surface of the samples by scanning electron microscopy (SEM) or, after replication and shadowing, by transmission electron microscopy (TEM). If the etchant has penetrated the bulk of the samples, thin sections can be microtomed and studied with TEM, if necessary after staining of the samples. There are, in principle, two different mechanisms for the etching:

1. Selective degradation involving chemical reaction with the polymer molecules, e.g. according to Refs. 18–20.

2. Selective dissolution of one of the components. This can be a useful method both for crystalline polymers, to separate low melting material from high melting material,<sup>21,22</sup> and for polymer blends.<sup>23</sup>

P(HBA-ET) copolymers have been etched with several proposedly selectively degrading etchants: *n*-propylamine,<sup>4–8</sup> anhydrous NH<sub>3</sub> at elevated pressures and plasma.<sup>16</sup> The authors of the latter work claim that the last two etchants selectively remove the PET component, although no clear evidence is presented. Joseph et al.<sup>8</sup> present data indicating a selective attack of *n*-propylamine on the ET-rich regions, viz., (a) homopolymer of PHBA is not etched within a few hours by *n*-propylamine and (b) the general appearance of electron micrographs of etched samples with varying HBA contents indicates a selective attack on the ET-rich domains.

PHBA is, however, a highly crystalline material—some authors claim 90% crystallinity<sup>24</sup>—and it is thus not representative of the state of this component in the copolymer with little or no 3-dimensional crystallinity. Prior to the work by Joseph et al.,<sup>8</sup> Chu and Wilkes<sup>25</sup> showed that *n*-propylamine breaks the ester linkages in PET. These authors verified the formation of *N,N*-dipropyl terephthalamide ( $T_m = 518$  K) and ethylene glycol by mass spectroscopy and thermal analysis.

The evidence hitherto presented in favor of the selectivity of the quoted etchants in the copolyesters is insufficient. This study has therefore been undertaken in order to obtain data related to the selectivity of etching of a number of etchants including *n*-propylamine and NH<sub>3</sub>. These data are here presented together with details of some preliminary electron microscopy work.

## EXPERIMENTAL

The polymers studied, kindly supplied by W. J. Jackson, Jr., Tennessee Eastman Co., are copolyesters composed of ethylene terephthalate (ET) and *p*-hydroxybenzoic acid (HBA) in two different molar ratios: 0.60 : 0.40 (HBA : ET) and 0.80 : 0.20 (HBA : ET). These polymers are here referred to as P(HBA-ET) 0.60 : 0.40 and P(HBA-ET) 0.80 : 0.20, respectively. A homopolymer of poly(ethylene terephthalate) (PET) (Arnite A04 102, Akzo Co., Netherlands) was used as "reference" material in this study. Information about the molecular structures of the copolyesters is given in Refs. 1–3.

Etching was carried out on 50  $\mu\text{m}$  films and on as-received pellets. The films were compression-molded in a hot stage between glass plates. The thickness of the films was carefully measured prior to etching. All samples were dried in vacuum at 333 K for 24 h prior to etching. The following etchants were used in these studies: concentrated  $\text{H}_2\text{SO}_4$ , 10% (w/w) aqueous solution of NaOH, 30% (w/w) aqueous solution of  $\text{NH}_3$ , 68% aqueous solution of ethylamine, *n*-propylamine (99%), *n*-butylamine (99%) and *n*-pentylamine (99%).

Etching was carried out at 296 K with  $\text{H}_2\text{SO}_4$  and the amines and at 338 K with NaOH and  $\text{NH}_3$ . After the etching, the samples were washed in an ultrasonic bath with distilled water and acetone and then dried in vacuum to constant weight. Electron spectroscopy for chemical analysis (ESCA) showed that this treatment sufficed to remove degradation products from the surface of the samples. The amount of material removed from the samples was determined by weighing the samples before and after etching and drying.

Infrared (IR) spectroscopy, differential scanning calorimetry (DSC), and ESCA were applied to determine the selectivity of the different etchants. Thin films or finely ground powder of the polymers were etched to obtain a favorable surface-to-volume ratio for the analyses.

DSC was performed in a Perkin-Elmer DSC-2, which was energy and temperature calibrated according to standard procedures. Prior to analysis, all samples were given the same thermal history in the DSC apparatus: heating to 590 K, retention at that temperature for 1 min, and finally cooling to 250 K at a rate of 40 K/min. The samples, weighing approximately 5 mg, were analyzed during a scan from 250 to 600 K at a rate of 10 K/min.

All these treatments were carried out in a nitrogen atmosphere to avoid degradation of the samples.

IR spectroscopy was performed using a Perkin-Elmer 580 B IR spectrometer equipped with an IR data station. Transmission spectra were obtained for powders and films of unetched and etched polymer dispersed in KBr. The selectivity of the etching was judged by measuring the absorbance at about 1700  $\text{cm}^{-1}$  ( $A_{1700}$ ), assigned to the carbonyl groups, and the absorbance at about 1460  $\text{cm}^{-1}$  ( $A_{1460}$ ), which is assigned to methylene groups.

ESCA spectra were recorded with a Leybold Heraeus ESCA/Auger LH 2000 spectrometer for films prior to etching and also after etching with about 10% of the material etched away. Etched and unetched pellets and films were examined in an ISI Super Mini SEM after gold-sputtering. Optical microscopy was performed on the degradation products formed after etching, with a Leitz Ortolux Pol BK equipped with a Mettler Hot Stage FP 82. Transmission electron microscopy was performed with a JEOL 2000 EX on microtomed samples covered with a 20 nm layer of carbon.

## RESULTS AND DISCUSSION

### Etching Rate Data

The etching rates ( $dL/dt$ ) on thin films were calculated from gravimetric data according to the equation

$$dL/dt = L_0 [w_0 - w(t)] / (2w_0 t) \quad (1)$$

where  $L_0$  and  $w_0$  are the thickness and weight of the sample prior to etching

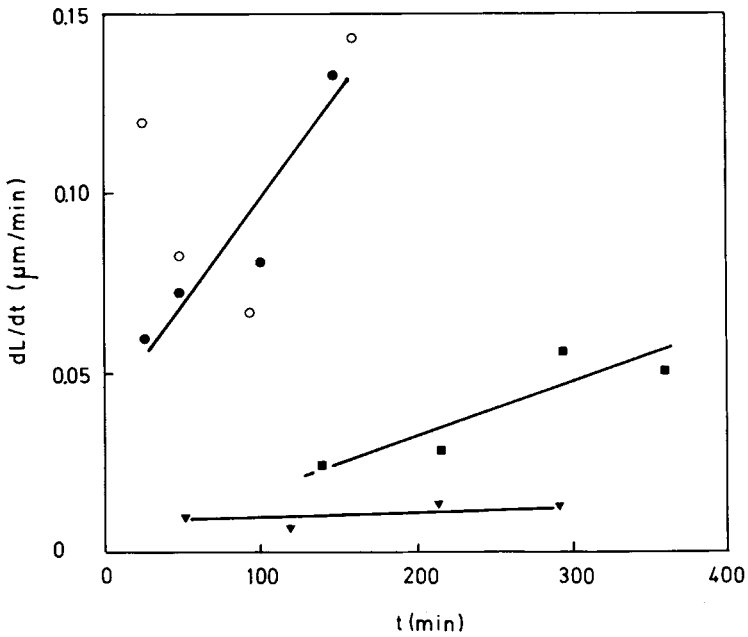


Fig. 1. The mean etching rate ( $dL/dt$ ) as a function of the etching time ( $t$ ) for film samples of P(HBA-ET) 0.60:0.40. The samples have been treated with different etchants: (○) ethylamine; (●) *n*-propylamine; (■) *n*-butylamine; (▼) *n*-pentylamine.

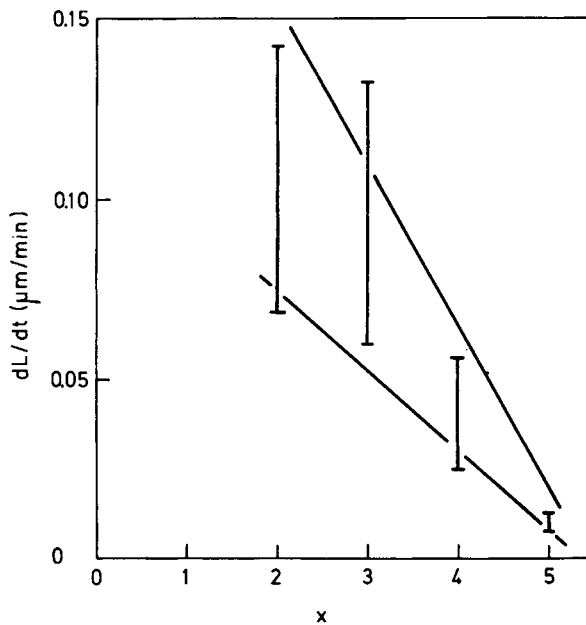


Fig. 2. The mean etching rate ( $dL/dt$ ) for samples of P(HBA-ET) 0.60:0.40 plotted as a function of the number of carbons in the *n*-alkylamine etchant.

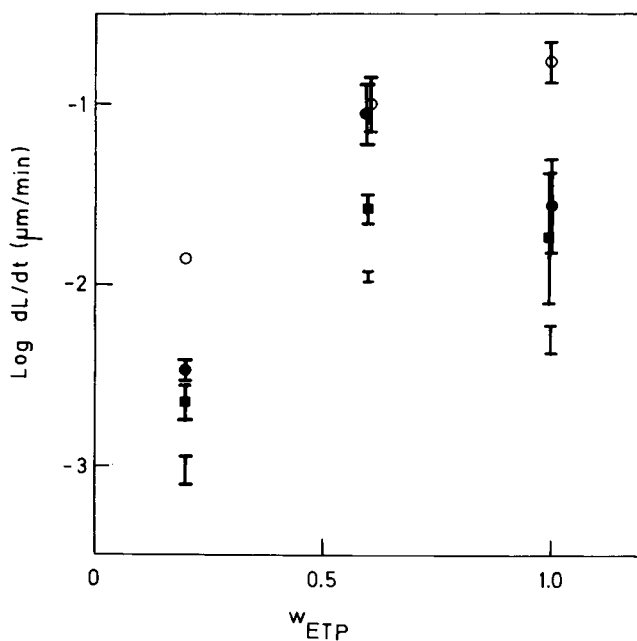


Fig. 3. The logarithm of the etching rate ( $dL/dt$ ) plotted as a function of the molar content of ethylene terephthalate ( $w_{ET}$ ) is the copolymer treated with the following etchants: (○) ethylamine; (●) *n*-propylamine; (■) *n*-butylamine; (▼) *n*-pentylamine.

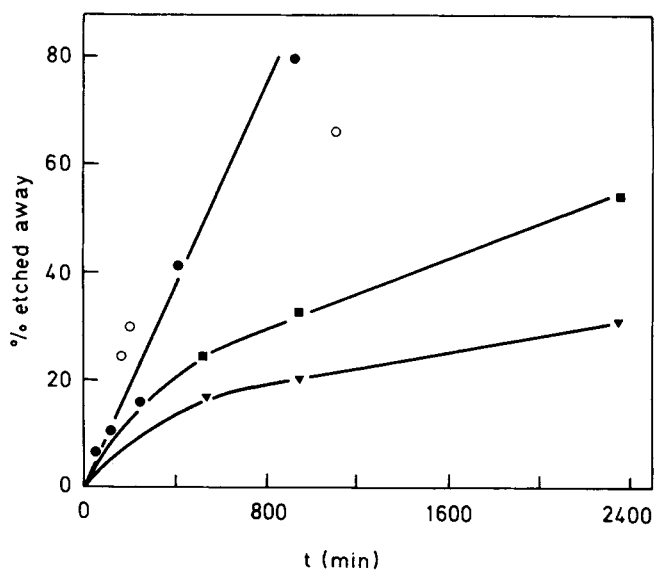


Fig. 4. Weight loss (% etched away) of P(HBA-ET) 0.60:0.40 powder plotted as a function of etching time ( $t$ ) for the following etchants: (○) ethylamine; (●) *n*-propylamine; (■) *n*-butylamine; (▼) *n*-pentylamine.

TABLE I  
 Etching Rate Data for P(HBA-ET) 0.60 : 0.40

Etchant	Temperature of etching (K)	Etching rate ( $\mu\text{m}/\text{min}$ )
Ethylamine	296	0.07-0.14
<i>n</i> -Propylamine	296	0.06-0.13
<i>n</i> -Butylamine	296	0.025-0.055
<i>n</i> -Pentylamine	296	0.0075-0.014
NaOH	338	0.025-0.045
NH <sub>3</sub>	338	0.03-0.05
H <sub>2</sub> SO <sub>4</sub>	296	2.5-4.5

and  $w(t)$  is the weight of the sample after  $t$  min of etching. For etched powder, the results are given as the percentage (w/w) material etched away vs. etching time. The etching rate data are presented in Figures 1-4 and Table I. Figure 1 shows that for the *n*-alkylamines the rate of etching increases with etching time (Fig. 1). This effect is pronounced for the shorter amines and appears to occur for all the amines tested with the exception of *n*-pentylamine. The etching rate is higher for shorter amines than for longer amines (Figs. 2 and 3), which may be due both to a higher penetration rate and to the higher mole content of amine groups per unit volume of the shorter amines. Figure 4 shows that on prolonged etching of powder the etching rate gradually decreases, indicating a buildup of nonetchable components in the solid residue.

Etching of the 0.80 : 0.20 copolymer with the *n*-alkylamines is about 1 order of magnitude slower than in the case of the 0.60 : 0.40 copolymer (Fig. 3), which is consistent with the idea of a selective attack on ET ester links. However, etching of quenched, fully amorphous PET is generally slower than etching of the 0.60 : 0.40 copolymer. An explanation is that etching is primarily dependent on the volume ("free volume") available for the etchant molecules to be transported into the bulk of the polymer prior to the degradation reaction. These observations are valid both for thin films and for finely ground polymer powders. It is also established from data shown in Figure 3 that the rate of etching of the 0.80 : 0.20 copolymer decreases with increasing length of the etchant (amine) molecule.

Table I summarizes all the etching rate data obtained for the 0.60 : 0.40 copolymer, including those obtained from etching with NaOH, NH<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>. Both NaOH and NH<sub>3</sub> have an etching power similar to that of *n*-propylamine and *n*-butylamine. Concentrated H<sub>2</sub>SO<sub>4</sub> seems to be too powerful as etchant. The samples treated with H<sub>2</sub>SO<sub>4</sub> degrade extensively, resulting in the formation of deep cracks all over the samples.

### DSC

The selectivity of the different etchants on the P(HBA-ET) 0.60 : 0.40 sample was judged on the basis of the intensity of the low temperature glass transition ( $\Delta C_{p,330}$ ) observed at about 330 K. This glass transition can be assumed to be assigned to the ET-rich phase.<sup>10</sup> The results presented in Figure 5 indicate a selective action of all the etchants used in removing the

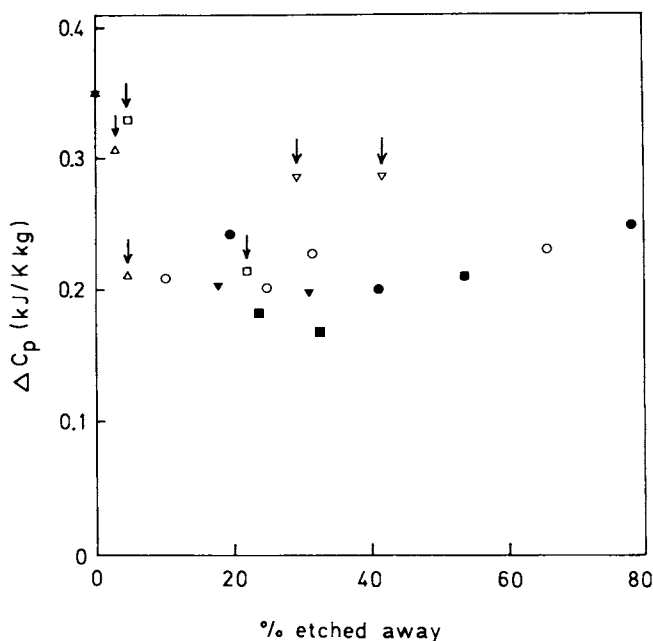


Fig. 5. The change in  $C_p$  accompanying the low temperature glass transition ( $\Delta C_{p330}$ ) plotted vs. the degree of etching (% etched away). Sample: P(HBA-ET) 0.60:0.40. Etchants: (○) ethylamine; (●) *n*-propylamine; (■) *n*-butylamine; (▼) *n*-pentylamine; (□) NaOH; (▼)  $H_2SO_4$ ; (△)  $NH_3$ . Film-shaped samples are indicated with arrows.

ET-rich (low- $T_g$ ) phase in the 0.60:0.40 copolymer. Most of the decrease in  $\Delta C_{p330}$  occurs in the early stages of etching, i.e., when less than 10% of the sample has been etched away. An approximately constant value of  $\Delta C_{p330}$  is observed after prolonged etching. The levelling-off value of  $\Delta C_{p330}$  obtained for the samples treated with the *n*-alkylamines corresponds to a decrease in the content of the low  $T_g$  material of about 40–50%. In the next section, these data are compared with IR data in order to obtain some information about the composition of the low  $T_g$  material.

The other etchants,  $H_2SO_4$ ,  $NH_3$ , and NaOH, seem to have about the same selectivity for ET-rich material as the *n*-alkylamines, despite some scatter in the data for the 0.60:0.40 samples etched with  $NH_3$  and NaOH (Fig. 5).

### IR Spectroscopy

The selectivity of the different etchants on the 0.60:0.40 copolymer was also explored with IR spectroscopy. The molar ratio of methylene groups to carbonyl groups ( $N_{me}/N_{ca}$ ) was determined from the absorbance values  $A_{1460}$  and  $A_{1700}$ , and the molar content of HBA [ $x$  (%)] in the etched samples was calculated according to the equation

$$N_{me}/N_{ca} = CA_{1460}/A_{1700} = (200 - 2x)/(200 - x) \quad (2)$$

The proportionality constant  $C$  was obtained from the IR spectrum of PET. The results of the IR measurements are presented in Figure 6.

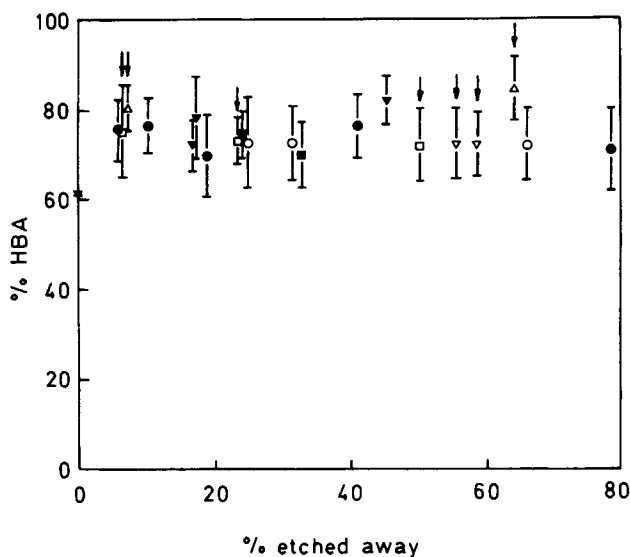


Fig. 6. HBA content (from IR, in mol %) in solid residue remaining after etching plotted vs. the degree of etching. Sample: P(HBA-ET) 0.60:0.40. Results are presented for samples (film samples are indicated with arrows) treated with the following etchants: (○) ethylamine; (●) *n*-propylamine; (■) *n*-butylamine; (▼) *n*-pentylamine; (□) NaOH; (▽) H<sub>2</sub>SO<sub>4</sub>; (△) NH<sub>3</sub>.

The content of HBA in the *n*-alkylamine-treated samples (0.60:0.40 copolymer) is approximately constant,  $73 \pm 7$  mol %, for degrees of etching higher than 10%, and it seems to be about the same for the different *n*-alkylamine treatments. Together with the information gained from DSC on the 0.60:0.40 copolymer (Fig. 5) showing that 40–50% of the low  $T_g$  material is removed by etching, this means that the average ET content of the removed material is about 70 mol %. The content of HBA in the 0.60:0.40 samples etched with the other etchants (NaOH, NH<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>) is about the same as for the samples etched with the *n*-alkylamines.

Results from IR spectroscopy on etched powder of the 0.80:0.20 copolymer presented in Table II also indicate a selective attack on the ET-rich material in this sample.

### ESCA

The carbon-to-oxygen ratio ( $C_{1s}/O_{1s}$ ) of the approximately 50 Å top layer of *n*-alkylamine-etched 0.60:0.40 copolymer samples was determined by ESCA from the integrated intensities of the  $C_{1s}$  and  $O_{1s}$  peaks located, respectively,

TABLE II  
Results from IR Spectroscopy on Etched Powder of 0.80:0.20 Copolymer

Etchant	% Etched away	% PHBA
Ethylamine	59.4	85.0
<i>n</i> -Propylamine	64.8	84.2–85.6
<i>n</i> -Butylamine	34.2	81.7–84.1



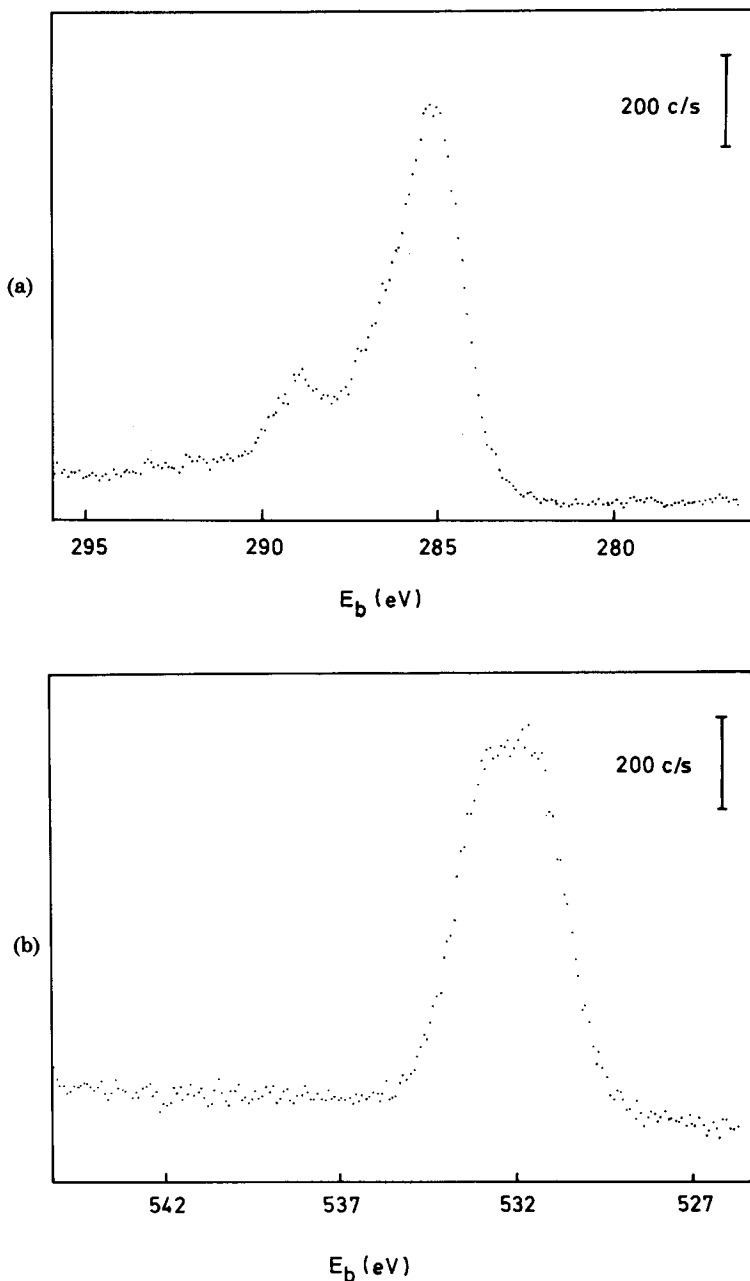


Fig. 7. Typical ESCA spectrum for P(HBA-ET) 0.60:0.40: (a) C<sub>1s</sub>; (b) O<sub>1s</sub>.

at 285 and 532 eV. A typical ESCA spectrum is shown in Figure 7. The molar content of HBA [ $x$  (%)] was calculated from the equation

$$C_{1s}/O_{1s} = (1000 - 3x)/(400 - 2x) \quad (3)$$

The results, all of them presented in Table III, confirm the excellent selectivity of all the *n*-alkylamines used on the 0.60:0.40 copolymer. The average

TABLE III  
 Results from ESCA

Sample	C <sub>1s</sub> /O <sub>1s</sub> <sup>a</sup>	C <sub>1s</sub> /O <sub>1s</sub> <sup>b</sup>	% HBA <sup>c</sup>
PHBA	3.50	—	100
PETP	2.50	2.65	0
P(HBA-ET) 0.60 : 0.40	2.93	2.94	60.6
P(HBA-ET) 0.60 : 0.40 etched with			
<i>n</i> -Ethylamine	—	3.49	99.7
<i>n</i> -Propylamine	—	3.25	85.8
<i>n</i> -Butylamine	—	3.40	94.9
<i>n</i> -Pentylamine	—	3.44	96.7

<sup>a</sup>Theoretical value.

<sup>b</sup>From ESCA.

<sup>c</sup>Calculated with eq. (3) using data by ESCA.

HBA content in the 50 Å top layer of the *n*-alkylamine-etched samples is 94 mol %.

### Analysis of Etching Products

A precipitate was observed in a solution of *n*-propylamine after its use as etchant on the 0.60 : 0.40 copolymer. Polarized light microscopy of the precipitate showed needlelike, optically uniaxial crystals which in the hot stage showed a premelting transition at 423 K and a major melting at 517 K. Studies with DSC confirmed these observations. Furthermore, the melting peak at 517 K recorded by DSC was very sharp, indicating that the substance is very pure. On cooling, a sharp crystallization exotherm was observed at 510 K. On reheating from room temperature, the major melting peak still occurred at 517 K, but the premelting transition at 423 K was absent. The melting point (517 K) recorded for the precipitate is in excellent agreement with the value reported for *N,N*-dipropylterephthalamide which has been isolated from the *n*-propylamine etchant after etching of PET.<sup>25</sup> IR analysis and gravimetric analysis of the precipitate confirm this finding.

### Electron Microscopy

Scanning electron micrographs of the 0.60 : 0.40 copolymer treated with the different etchants are shown in Figure 8. The features of the micrographs are as follows:

—Samples etched with H<sub>2</sub>SO<sub>4</sub> and NH<sub>3</sub> exhibit globular structures of two different sizes, 1–2 μm and 0.1 μm [Figs. 8(b) and (c)]. The surface of the samples etched with H<sub>2</sub>SO<sub>4</sub> is cracked, and the surface displayed in Figure 8(b) originates from a crack.

—The sample etched with NaOH [Fig. 8(d)] exhibits a Swiss-cheese structure with spherical holes, 1–2 μm in diameter.

—Samples etched with *n*-propylamine display a similar Swiss-cheese morphology [Figs 8(e)–(h)]. The sample etched for a short time displays spherical holes with a diameter of 1–2 μm [Fig. 8(e)]. The holes grow together on

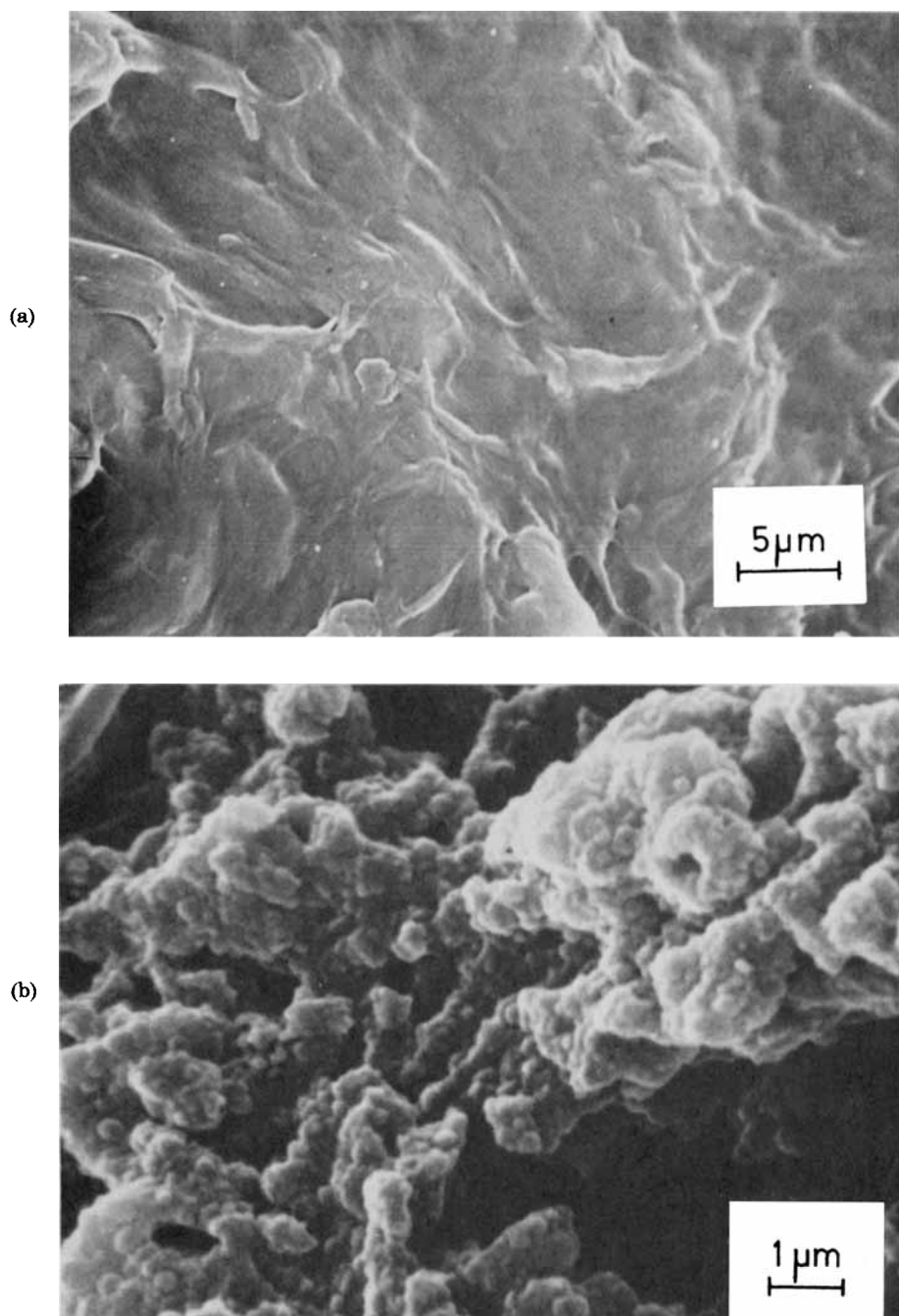


Fig. 8. Scanning electron micrographs of P(HBA-ET) 0.60:0.40: (a) prior to etching; (b) etched with  $\text{H}_2\text{SO}_4$ ; (c) etched with  $\text{NH}_3$ ; (d) etched with  $\text{NaOH}$ ; (e) etched with *n*-propylamine, 6.5% of the material is etched away; (f) etched with *n*-propylamine, 19% is etched away; (g) etched with *n*-propylamine, 41.2% is etched away; (h) etched with *n*-propylamine, 79.2% is etched away; (i) etched with ethylamine, 25.0% is etched away; (j) etched with *n*-butylamine, 24.2% is etched away; (k) etched with *n*-pentylamine, 17% is etched away.

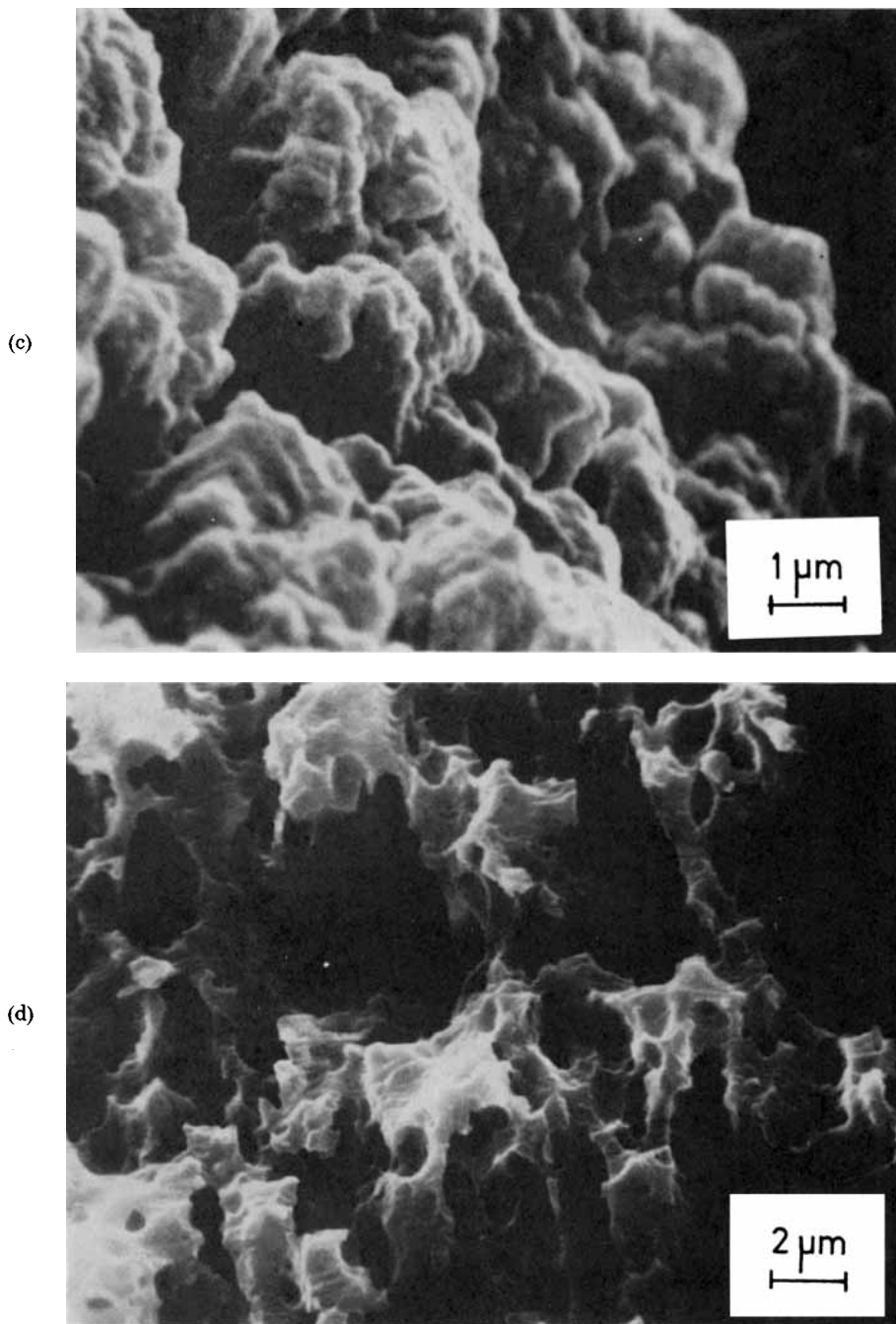


Fig. 8. (Continued from the previous page.)

prolonged etching forming holes of 5–10  $\mu\text{m}$  in diameter [Figs. 8(e)–(h)]. However, the 1–2  $\mu\text{m}$  “primary” holes are also easily distinguished in the samples etched for a long time, demonstrating that this morphology is genuine.

—Samples etched with the other *n*-alkylamines also display the Swiss-cheese structure described in the foregoing item.

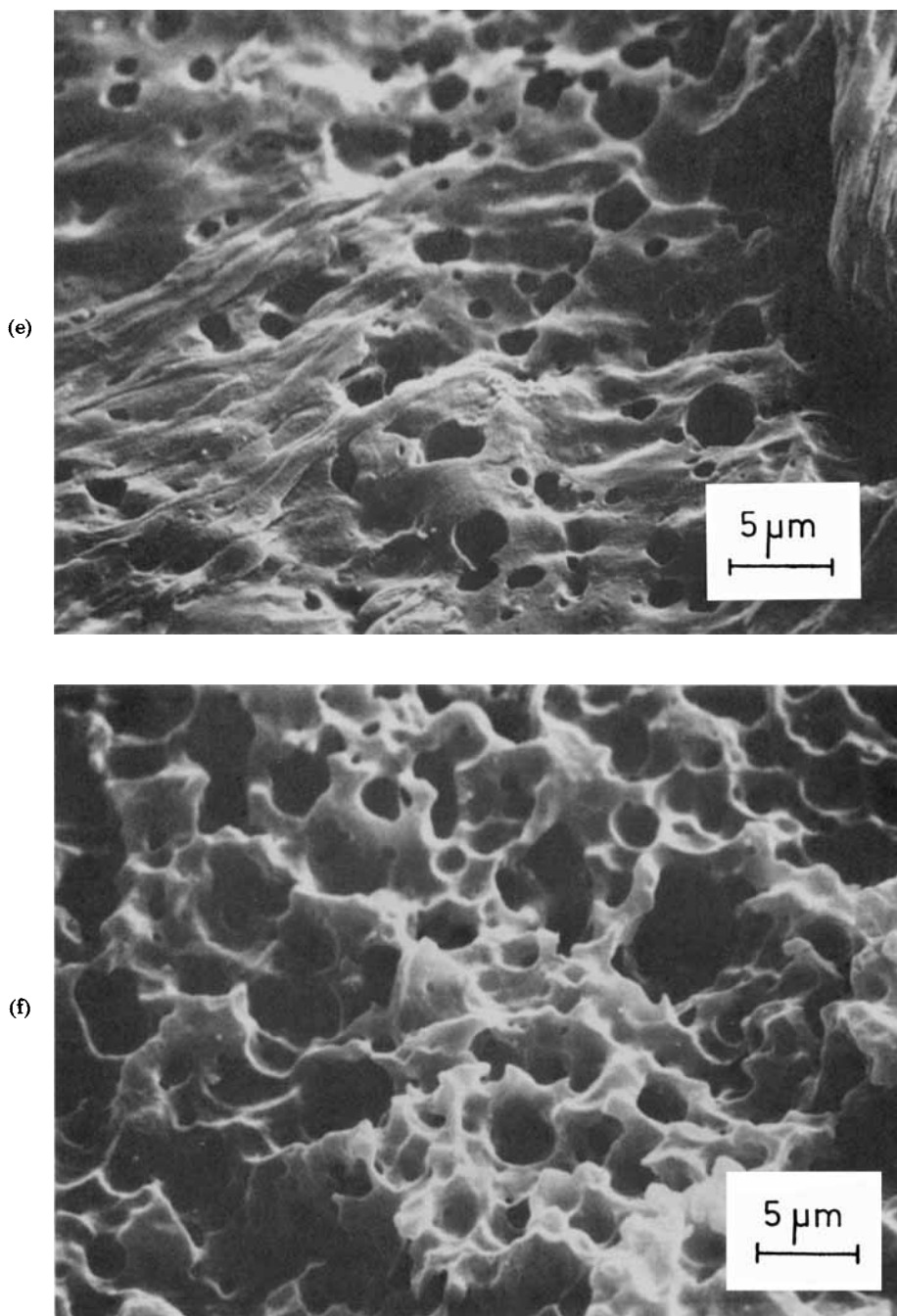


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The transmission electron micrographs of the 0.60 : 0.40 copolymer samples shown in Figure 9 are consonant with the two-phase morphology evident from SEM. There is a close resemblance in size and shape between the holes observed in the 0.60 : 0.40 copolymer samples etched with NaOH or *n*-alkylamines and the distinct, dark regions observed in the transmission

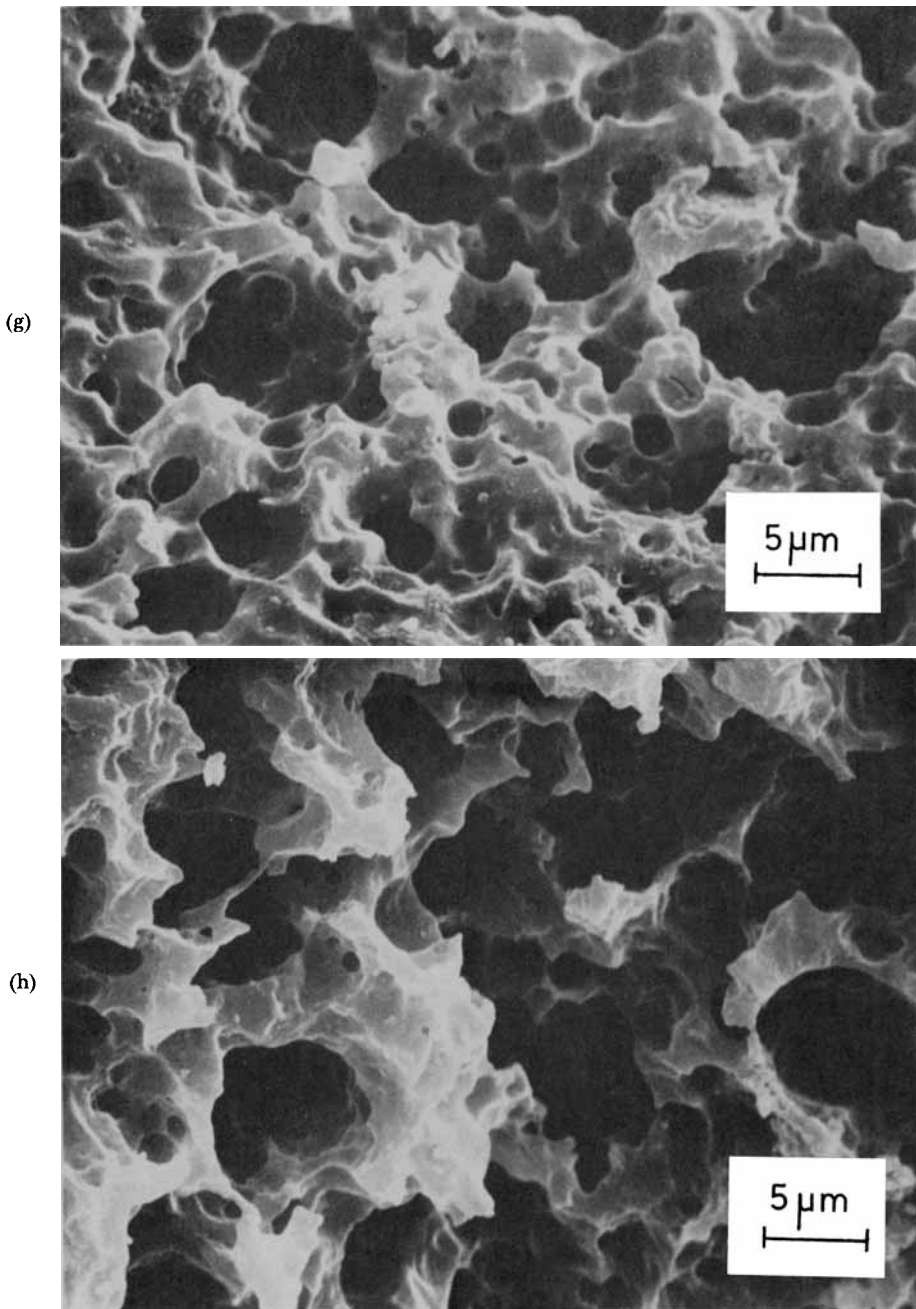


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electron micrographs [cf. Figs. 8(d)–(k) and 9(a)]. Figure 9(b) shows that the discontinuous, dark phase is softer than the continuous, bright phase. It is reasonable to assume that the discontinuous and etch-sensitive phase is rich in ET. Thus, SEM indicates that all the etchants studied except  $\text{NH}_3$  and  $\text{H}_2\text{SO}_4$  selectively remove the ET-rich phase in the P(HBA–ET) 0.60:0.40

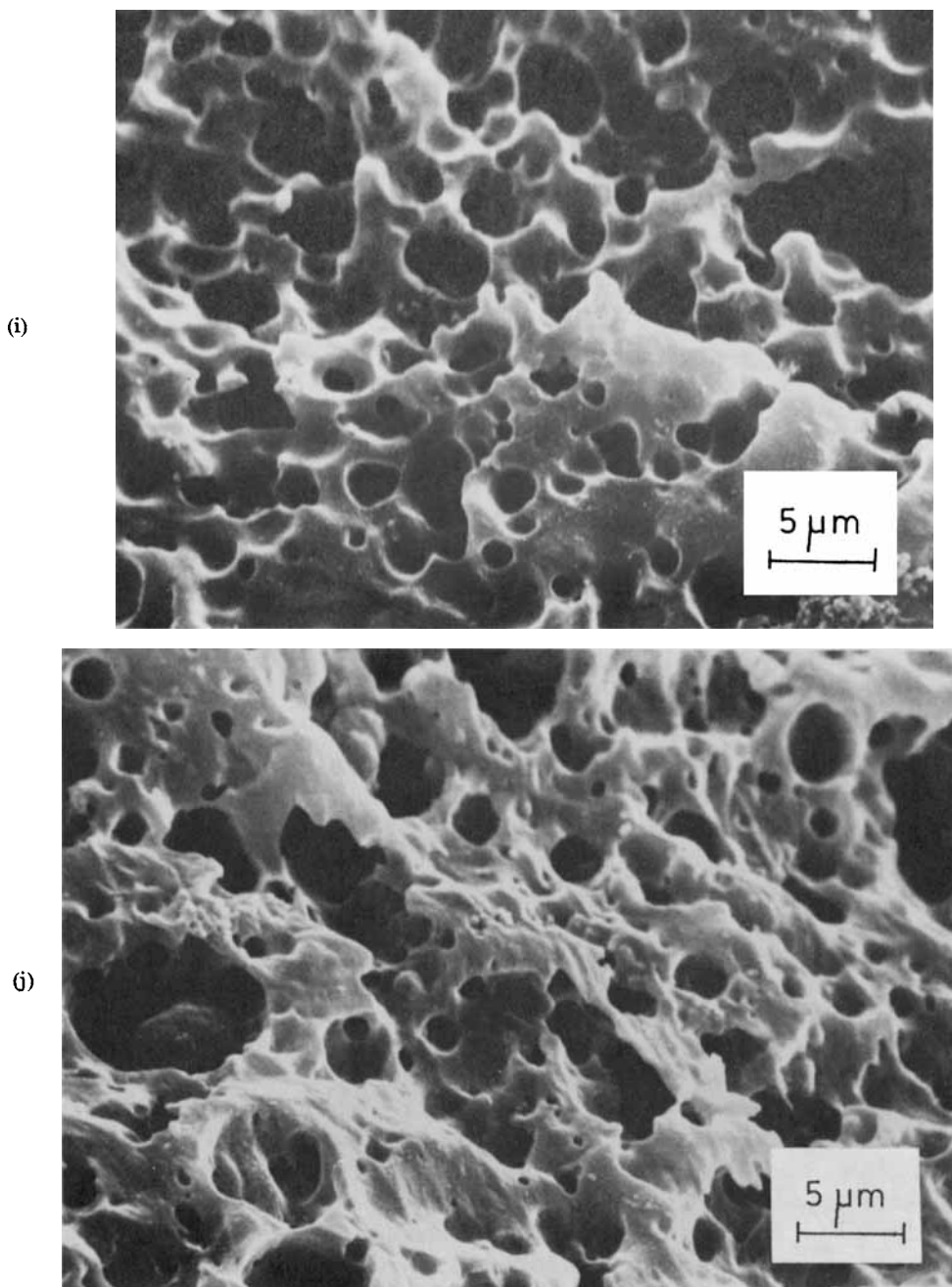


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copolymer. The continuous HBA-rich phase in the 0.60:0.40 copolymer displays a fine-textured substructure which is only revealed by TEM [Fig. 9(b)].

The P(HBA-ET) 0.80:0.20 copolymer displays a finer textured structure than the 0.60:0.40 copolymer [Fig. 10(a)]. There is no two-phase structure of micrometer-size consistent with earlier observations by Zachariades et al.<sup>16,17</sup>

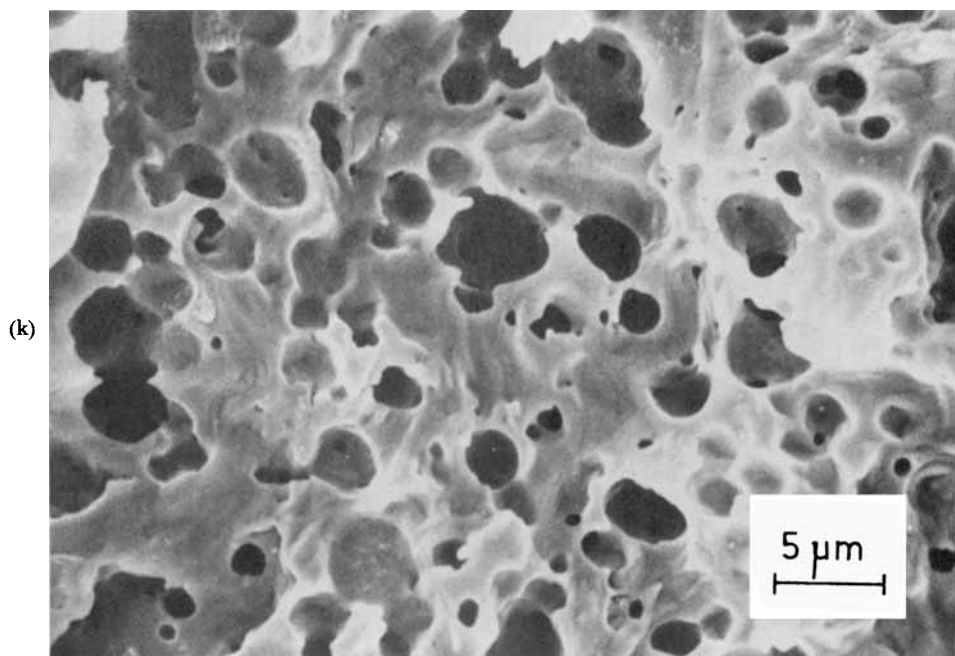


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The transmission electron micrographs shown in Figure 10(a) may indicate the existence of lamellar structures on a submicrometer scale. The SEM studies of possibly selectively etched samples reveal relatively little information about the morphology [Figs. 10(b) and (c)], although there are some traces of lamellar-shaped structures in the ethylamine-etched samples.

### CONCLUSIONS

DSC, IR, ESCA, macroscopic etching rate measurements, analysis of the etching products and electron microscopy conclusively show that short-chain *n*-alkylamines, i.e., ethylamine, *n*-propylamine, *n*-butylamine, and *n*-pentylamine, selectively remove (etch) the ET-rich material in P(HBA-ET) with molar composition 0.60:0.40. It is demonstrated by DSC that these etchants selectively remove the low- $T_g$  material, which indicates that this material is rich in ET. IR spectroscopy shows that these etchants penetrate the bulk of the 0.60:0.40 copolymer and degrade and remove interior ET-rich material. ESCA demonstrates the excellent selectivity on the 0.60:0.40 copolymer of the *n*-alkylamine etchants; the 50 Å top layer of the etched samples contains 95 mol % HBA. It is demonstrated by SEM and TEM that the ET-rich phase in the 0.60:0.40 copolymer is discontinuous and forms 1–2  $\mu\text{m}$  spherical particles. This is in perfect agreement with reports by Joseph et al.<sup>5–8</sup> SEM is a very useful tool for characterization of the structure. However, both phases, i.e., the ET-rich globules and the continuous HBA matrix have a substructure which is revealed only by TEM.  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$  both give ambiguous results and should not be used as etchants for this



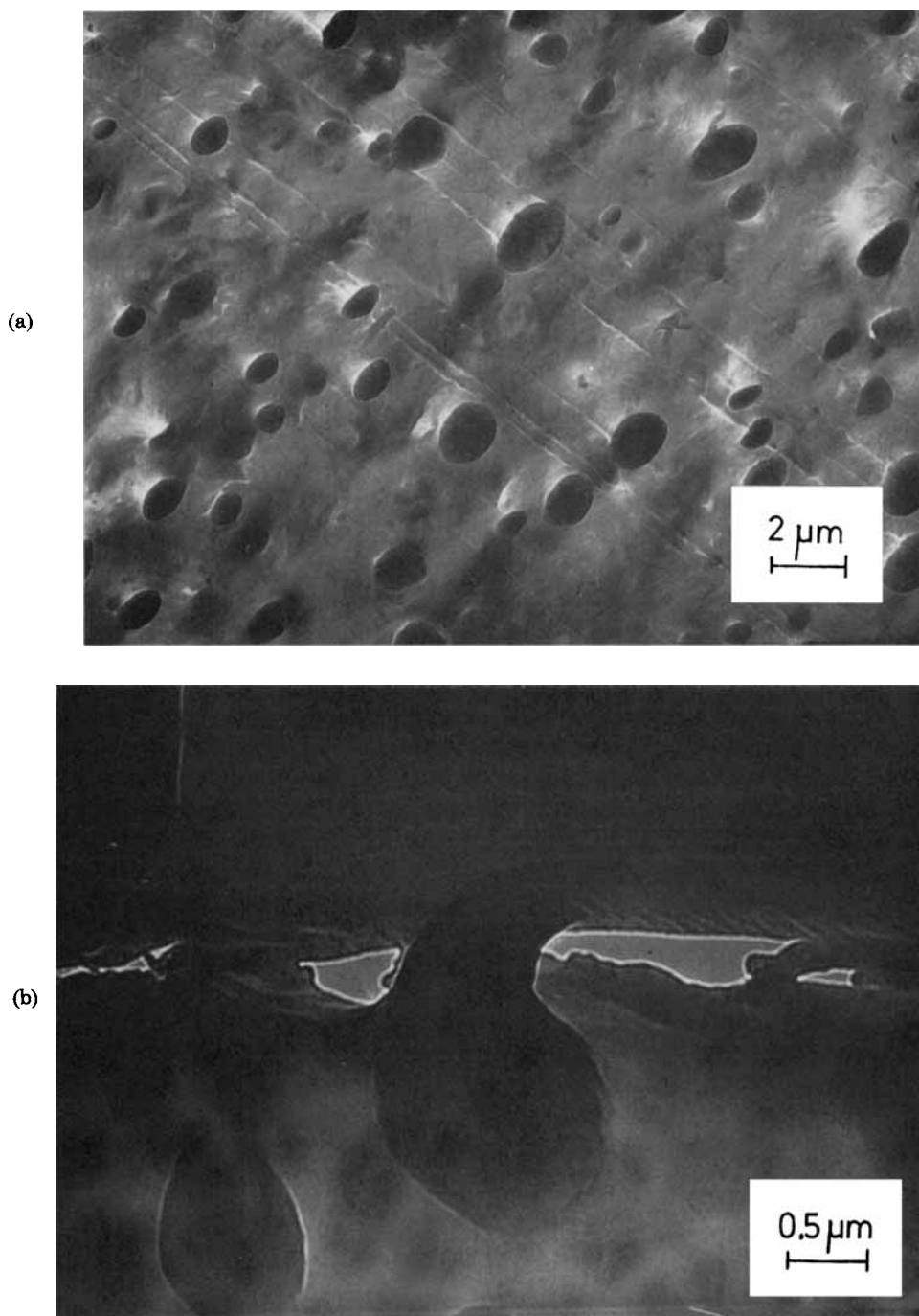


Fig. 9. Transmission electron micrographs of P(HBA-ET) 0.60 : 0.40. Note the shearing with the microtome of the "dark" phase in Figure 9(b).

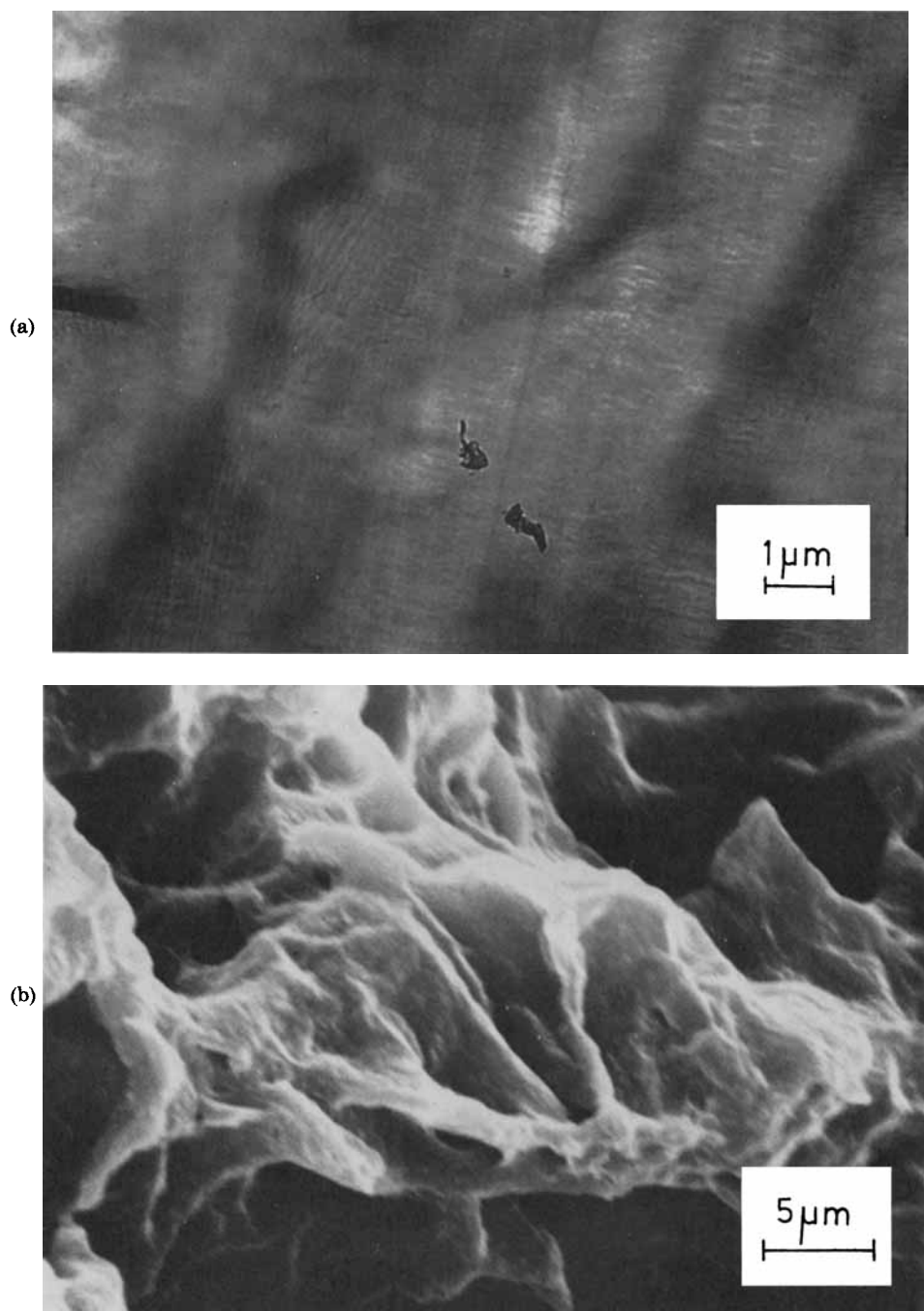


Fig. 10. Electron micrographs of P(HBA-ET) 0.80:0.20: (a) by TEM; (b) by SEM on sample etched with ethylamine (47% is etched away); (c) by SEM on sample etched with *n*-propylamine (47% is etched away).

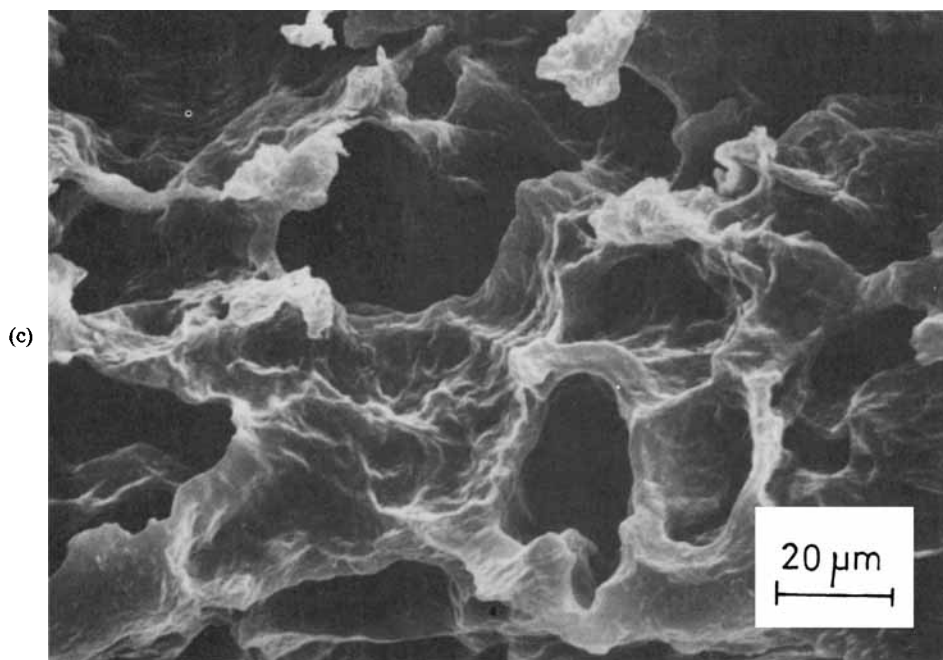


Fig. 10. (Continued from the previous page.)

copolymer. NaOH reveals the same type of morphology in the copolymer as do the *n*-alkylamines.

It is indicated by IR that the *n*-alkylamine etchants also degrade (etch) the P(HBA-ET) 0.80 : 0.20 copolymer selectively; but the morphology is fine-textured, and SEM is not an ideal tool for morphology studies of this material. TEM of replicate of etched samples is presumably a more suitable method. Such studies are at present being carried out in this laboratory and will be reported on in a upcoming paper.

The reported studies have been sponsored by The National Swedish Board for Technical Development (STU), Grant 84-3455, The Swedish Natural Science Research Council (NFR), Grant K-RT 1910-100, and the Jacob Wallenberg Foundation. The authors wish to thank Dr. W. J. Jackson, Jr., Tennessee Eastman Co., for providing the copolyesters studied, and Dr. Hans Bertilsson, University of Luleå, Sweden for valuable discussions.

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Received September 9, 1986

Accepted November 3, 1986