

Effects of Modifier Addition and Temperature Variation in SFE of Polymeric Materials

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Abstract

The effects of modifier addition and temperature variation on the supercritical fluid extraction of nylon-6 and poly(1,4-butylene terephthalate) samples are discussed. The modifiers studied include hexane, chloroform, methanol, and benzene. The influence of experimental parameters, such as extraction temperature and pressure, static time, and supercritical fluid flow rate, are investigated systematically with both pure and modified carbon dioxide. The addition of a suitable modifier results in significantly enhanced extraction rates, particularly at low extraction temperatures. A simple experimental setup for the introduction of additional volumes of modifier during the extraction was developed and evaluated. Guidelines for the optimization of the supercritical fluid extraction of polymeric samples are given.

Introduction

Supercritical fluid extraction (SFE) has been recognized as an important alternative to extractions using liquid solvents (1–3). The most widely used supercritical fluid in SFE is carbon dioxide because of its reasonable critical properties, low toxicity, chemical inertness, acceptable price, and capability to dissolve numerous compounds ranging in polarity from nonpolar to moderately polar. However, supercritical carbon dioxide does not have sufficient solvent strength for the extraction of polar analytes, and it is a poor choice for overcoming the interaction between analytes and the matrix.

The extracting capability of carbon dioxide can be greatly enhanced with modifiers (4). The effects of modifiers on SFE efficiency have been the subject of a number of investigations. Numerous compounds ranging from nonreactive modifiers (methanol, water, dichloromethane, organic amines, and acids) to reactive modifiers (ion pairing agents and derivatizing agents) have been used as modifiers in analytical SFE of mainly environmental samples (5–13). Unfortunately, the role of modifiers in analytical SFE is still not well understood. The selection of

modifiers and their concentrations is still highly empirical. This is especially true for the SFE of polymeric samples, for which very few applications of modifiers have been reported (14,15).

SFE has been increasingly used for polymeric applications. Bartle and co-workers (16) derived a model for diffusion-limited extractions, assuming that the matrix particles are spheres of a well-defined size and the initial distribution of the solutes within the spheres is uniform. Cotton and co-workers (17) and Kueppers and co-workers (18) investigated temperature effects in SFE and found that higher extraction efficiency could be obtained at elevated temperatures. Via and co-workers (19) fractionated low molecular weight, high-density polyethylene wax at different temperatures with three different supercritical fluids. They found that higher temperatures at constant density yielded extracts with higher molecular weights. Similar work on fractionation of ethylene–methylacrylate copolymers with SFE was reported by Pratt and co-workers (20).

Optimization of SFE methods with modified fluids frequently requires testing various modifiers at different concentrations as well as determining optimal temperature and pressure conditions. In the extraction of polymeric materials, the extraction pressure is relatively simple to select. High extraction pressures are generally advantageous. However, selection of optimal temperature conditions is complicated. Increasing the extraction temperature will, on the one hand, decrease the density of the supercritical fluid. On the other hand, it can also improve the kinetics of mass transfer of the analyte from the matrix to the supercritical extractant and increase vapor pressure of the analyte. Very often, the effects of a temperature variation will also depend on the extraction pressure and the properties of the analytes and matrix (14). Temperature effects get even more complicated when modifiers are used. Yang and co-workers (21) tested the combined effects of modifier addition and temperature variation for the extraction of polycyclic aromatic hydrocarbons from environmental samples. They found that, for these samples, the combination of a suitable modifier and elevated temperature was most effective. Unfortunately, to our knowledge, for the extraction of polymeric materials, modifier effects and the combined influence of modifier and temperature have not been investigated in detail until now.

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In this study, four modifiers with different chemical properties were tested at various temperatures for the extraction of two polymeric materials, nylon-6 and poly(1,4-butylene terephthalate) (PBT). The effects of temperature when either pure or modified carbon dioxide was used are compared. The roles of modifier addition and temperature variation in the extraction of polymeric samples are discussed. A simple experimental setup for the introduction of additional volumes of modifier during SFE was proposed and evaluated.

Theory

In a previous publication (14) we applied the two-film theory for resistance to mass transfer to qualitatively describe the kinetics of extraction in SFE. In that work, it was shown that the rate-limiting step for the SFE of polymer additives from polymeric samples was either diffusion in the polymer particles or transport of the extracted components out of the extraction cell. These two steps are related to two parameters: diffusion and solubility. Which of these two parameters actually governs the extraction kinetics can be investigated by studying the influence of pressure or temperature on the extraction rate. If the rate-limiting parameter is solubility of the components in the su-

percritical fluid, an increase in pressure will increase the extraction rate. If, on the other hand, the rate-limiting parameter is diffusion of the analytes in the polymer particles, extraction pressure will have little or no effect on the extraction rate for SFE (14). Apart from pressure, other parameters also affect the kinetics in SFE. Among these, temperature and type and concentration of the modifier appear to be the most important parameters.

The strategy for optimizing the conditions for the extraction of polymeric materials depends on which step in the extraction is the rate-limiting step. If the rate-limiting step is diffusion of the analytes in the polymer particles, then the extraction rate can be increased by increasing the extraction temperature because this results in increased diffusion in the polymer particles. The addition of a suitable modifier that swells the polymer is another method for enhancing diffusion in the polymer particles. Evidently, the extraction rate can also be increased by decreasing the particle size of the polymer. If the rate-limiting parameter for extraction is the solubility of the analytes in the supercritical fluid, extraction rates can be increased by increasing the solvent strength of the supercritical extractant. One way to achieve this is by introducing modifiers. Moreover, the extraction rate can also be increased by increasing the extraction pressure, by decreasing the extraction temperature, or by increasing the supercritical fluid flow rate. A general strategy for optimizing

experimental parameters in the extraction of polymeric materials is shown in Figure 1. As already mentioned, pressure effects are relatively easy to understand. Experimental pressure should be selected so that it is sufficiently high. However, the selection of temperature and modifier type and concentration is much more complicated because these parameters are highly matrix- and analyte-dependent, and their effects on extraction are often interrelated.

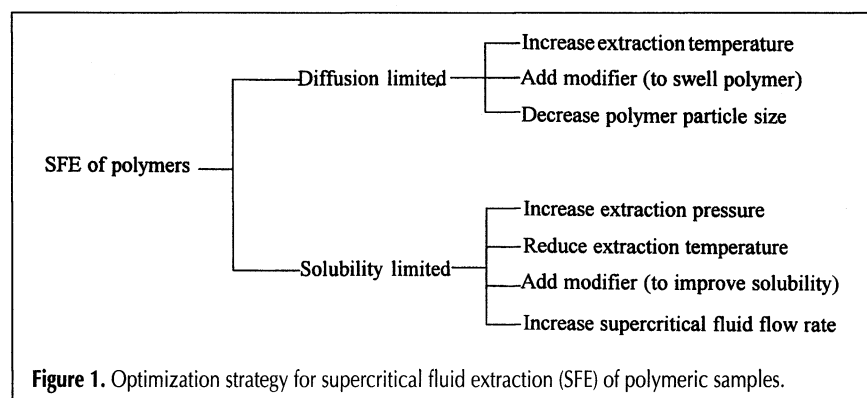


Figure 1. Optimization strategy for supercritical fluid extraction (SFE) of polymeric samples.

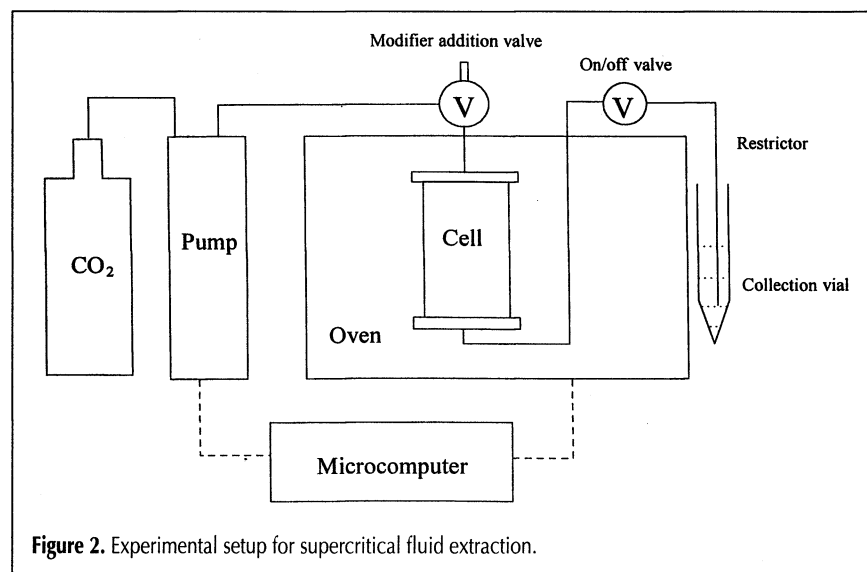


Figure 2. Experimental setup for supercritical fluid extraction.

Experimental

The polymeric samples used in this study, nylon-6 (glass transition temperature, $T_g = 62.5^\circ\text{C}$) and PBT ($T_g = 66^\circ\text{C}$) were purchased from Aldrich (Milwaukee, WI). It should be emphasized here that T_g values under supercritical carbon dioxide conditions can be significantly different from the data specified above. The polymeric samples were ground by milling under liquid nitrogen before extraction.

SFE experiments were performed with a modified Carlo Erba SFC 3000 capillary supercritical fluid chromatograph (Carlo Erba; Milan, Italy). A 3-mL stainless steel cell (Suprex; Pittsburgh, PA) was fitted with hand-tight connectors (Suprex) for easy installation. Stainless steel frits (3 μm) were

located at either end of the extraction cell. Fused-silica capillaries (20- or 50- μm i.d.) were used as restrictors. To enable static extraction, an on/off valve (Valco; Schenkon, Switzerland) was installed directly behind the extraction cell. The extracted material was collected by inserting the restrictor outlet into a glass vial (10 cm \times 1-cm i.d.) that contained 5 mL dichloromethane. This vial was changed every 30 min, and an internal standard was added. Eicosane and tetracontane were selected as the internal standards for the extracts from nylon-6 and PBT, respectively. After collection, dichloromethane was evaporated under a gentle flow of nitrogen, and the extracted material was redissolved in a suitable amount of chloroform. Quantitative trapping in the liquid collection trap was confirmed by spiking known amounts of the analytes onto clean sand and extracting them for 30 min (5 min static plus 30 min dynamic) with pure carbon dioxide at 150°C and 300 bar and at a supercritical fluid flow rate of 550 mL/min (gas flow measured at ambient conditions). The trapping efficiencies obtained this way were never lower than 92%.

For SFE extractions, approximately 1.9 g nylon-6 or 1.6 g PBT was weighed into the extraction cell. A static time of 20 min was used before dynamic extraction. The highest extraction temperature tested for both polymers was 170°C. At higher temperatures the restrictor often became blocked because of partial melting of the polymers. The carbon dioxide used in the experiments had a purity of 99.996% (Intermar; Breda, The Netherlands). Soxhlet extractions were performed to produce frames of reference. Extraction efficiencies for SFE were calculated relative to the Soxhlet data. For Soxhlet extractions of both polymers, sample sizes of approximately 2 g were placed in the Soxhlet extractor and extracted for 36 h. Methanol and chloroform were used as the Soxhlet extraction solvents for nylon-6 and PBT, respectively (22).

To introduce additional modifiers during SFE extraction, a

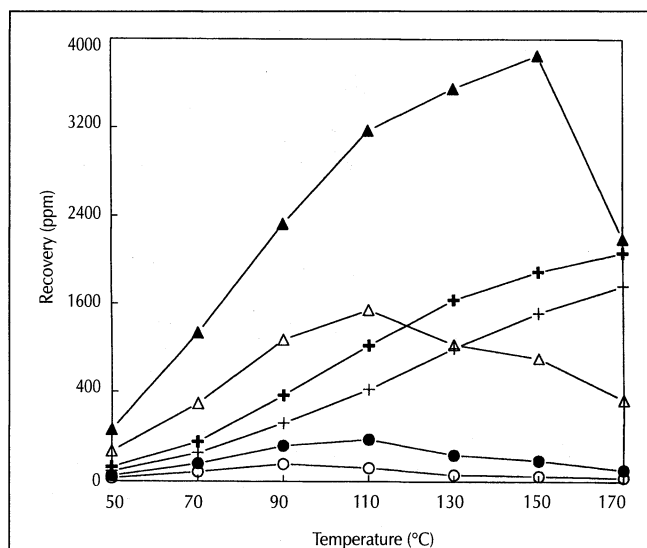


Figure 3. Effects of temperature on the supercritical fluid extraction. Conditions: extractant, pure carbon dioxide; extraction pressure, 300 bar; static time, 20 min; dynamic time, 30 min or 2 h; restrictor, 70-cm \times 50- μm fused-silica capillary; collection solvent, 5 mL dichloromethane. Key: — \triangle —, caprolactam (30 min); — \square —, caprolactam (2 h); — \circ —, dimer (30 min); — \blacktriangle —, dimer (2 h); — \circ —, trimer (30 min); — \bullet —, trimer (2 h).

liquid chromatographic (LC) injection valve (CH 6214, Valco) with a sample loop of 0.1 mL was installed before the extraction cell. The experimental setup is shown schematically in Figure 2.

The extracted components were analyzed using a gas chromatograph equipped with an on-column injector and a flame-ionization detector (GC 8000 series, Carlo Erba). For the analysis of the extracts from nylon-6, a DB-1 column (15 m \times 0.32-mm i.d., 1- μm film thickness) purchased from J&W (Folsom, CA) was used. The initial temperature for analysis was 40°C. The temperature was then programmed to 250°C at 20°C/min. An HT SimDist-CB column (10 m \times 0.53-mm i.d., 0.17- μm film thickness) purchased from Chrompack (Middelburg, The Netherlands) was used for the analysis of the extracts from PBT. The initial temperature for the gas chromatographic separation was 40°C. The temperature was then programmed to 400°C at 20°C/min.

Many of the extractions were repeated three times. For the repeated experiments, the relative standard deviation was within 5% with pure carbon dioxide and within 9% when modifiers were used.

Results and Discussion

Effects of temperature using pure carbon dioxide

In the extraction of polymeric materials, the extraction rate is controlled by either the rate of diffusion of the analytes in the polymer or the solubilities of the analytes in the supercritical fluid. When pressure was increased from 150 to 300 bar at 50°C, no considerable variation in the extraction yields of the analytes from the polymers studied was observed. This is

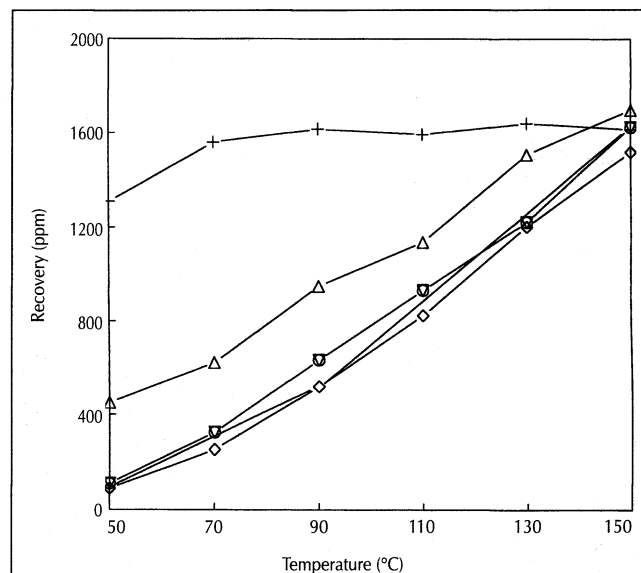
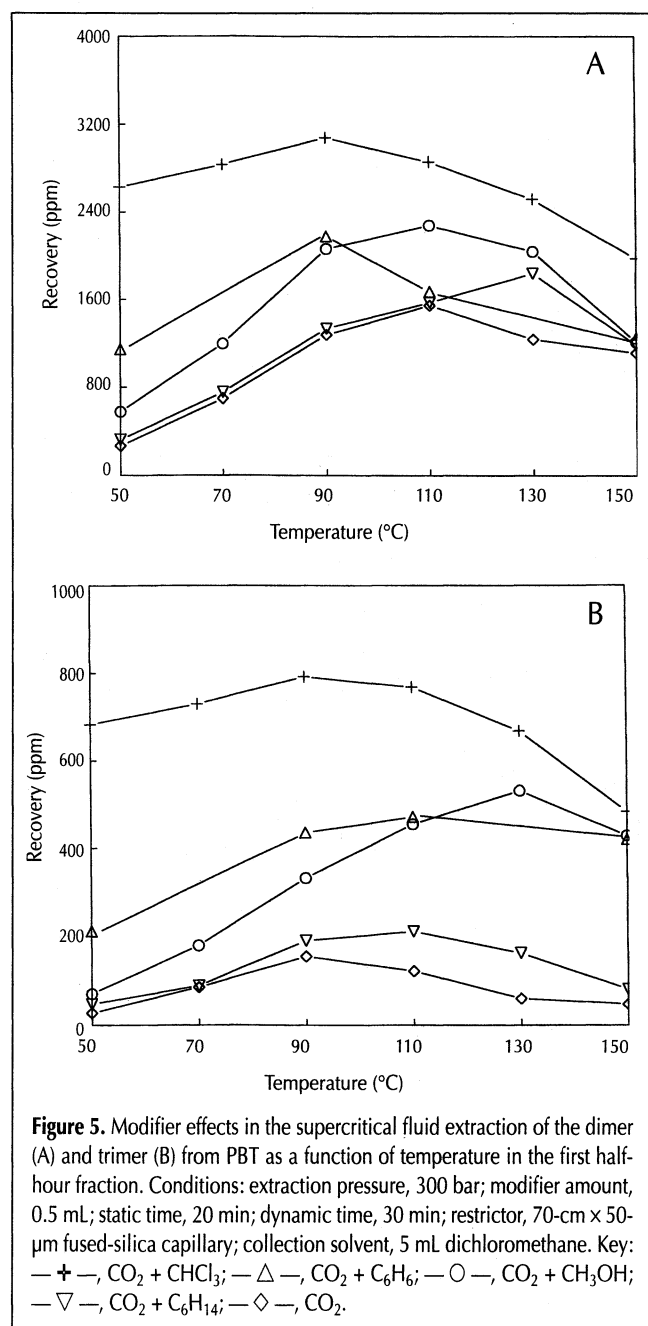


Figure 4. Modifier effects in the supercritical fluid extraction of caprolactam from nylon-6 as a function of temperature in the first half-hour fraction. Conditions: extraction pressure, 300 bar; modifier amount, 0.5 mL; static time, 20 min; dynamic time, 30 min; restrictor, 70-cm \times 50- μm fused-silica capillary; collection solvent, 5 mL dichloromethane. Key: — \triangle —, CO₂ + CH₃OH; — \square —, CO₂ + CHCl₃; — \circ —, CO₂ + C₆H₆; — ∇ —, CO₂ + C₆H₁₄; — \diamond —, CO₂.

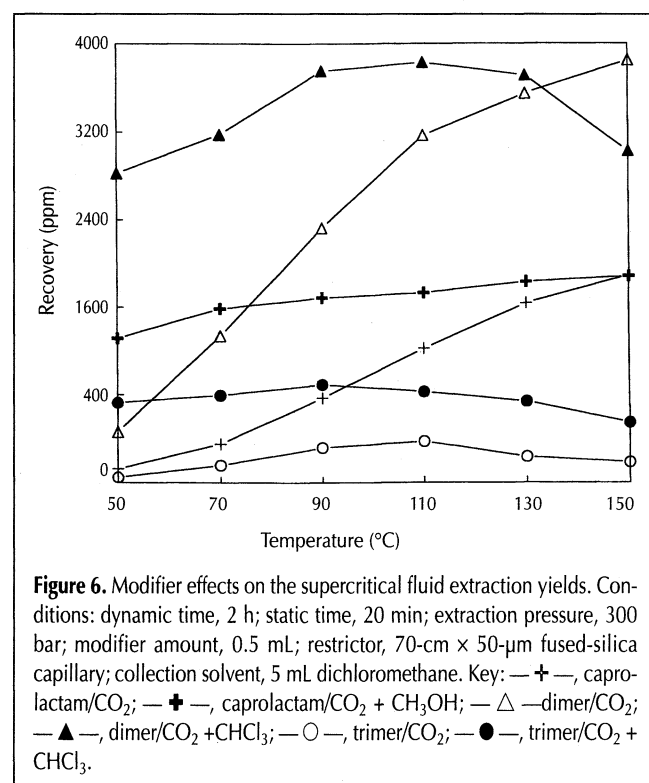
because at 50°C the density of the supercritical fluid is relatively high, even at a mild pressure of only 150 bar ($\rho = 0.701 \text{ g/mL}$). As diffusion of the components in the polymer is relatively slow at this low temperature, the mass flow of components diffusing to the polymer surface is low. Molecules diffused to the surface are rapidly transferred to the supercritical fluid and carried out by the flow of high-density carbon dioxide. Under these conditions the extraction rate is determined by diffusion of the analytes in the polymer particles.

As discussed in the Theory section, diffusion coefficients of analytes in polymer particles can be increased by either increasing the extraction temperature or adding a suitable modifier. To investigate the influence of temperature, nylon-6 and PBT were extracted at different temperatures at a pressure of 300 bar. The results are illustrated in Figure 3. The highest temperature tested for both polymers is 170°C. At higher temperatures, frequent



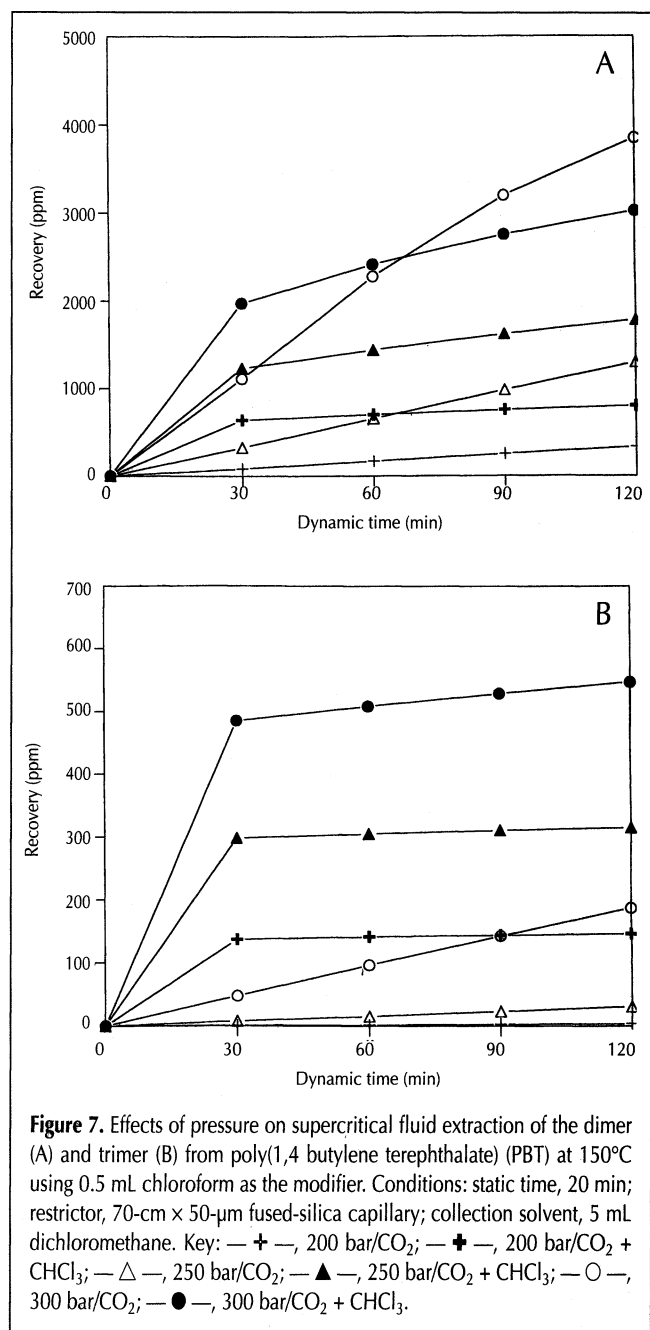
blocking of the restrictor occurred because of partial melting of the polymers. For nylon-6, the efficiency at which caprolactam was extracted increased considerably when the temperature was raised from 50°C to 170°C at 300 bar (Figure 3). No abrupt changes in extraction recoveries for both polymers were observed around their normal glass transition temperatures, which suggests that the T_g values under supercritical carbon dioxide conditions are lower than the normal T_g value.

It can be seen from Figure 3 that the effects of temperature in the SFE of polymeric materials are both matrix- and analyte-dependent. It appears that the effects of temperature on the SFE of PBT are more complicated than on the extraction of nylon-6. In contrast to the continuous increase in yield for the extraction of caprolactam from nylon-6, the total extraction recovery for the dimer obtained in 2 h first increased considerably when the temperature was raised from 50°C to 150°C and then decreased at temperatures exceeding 150°C. Apparently, at low temperatures the rate-limiting parameter is diffusion of analytes in the polymer particles. At elevated temperatures diffusion will be enhanced. However, at the same time, the density of the supercritical fluid will decrease. Above a certain temperature, diffusion of the analytes in the polymer particles is relatively fast while at the same time the density of the supercritical fluid is low. At this time, solubility of the components in the supercritical fluid becomes the rate-limiting parameter. Solute molecules diffused to the surface can no longer be rapidly eluted by the flow of the low-density extractant. Increasing temperature at constant pressure will further decrease the solubility of the relatively nonvolatile oligomers in the supercritical extractant, thus decreasing the extraction rate for SFE. The temperature at which this occurs depends on the properties of both the analyte and the matrix as well as on the extraction pressure. Similar effects of temperature were also ob-

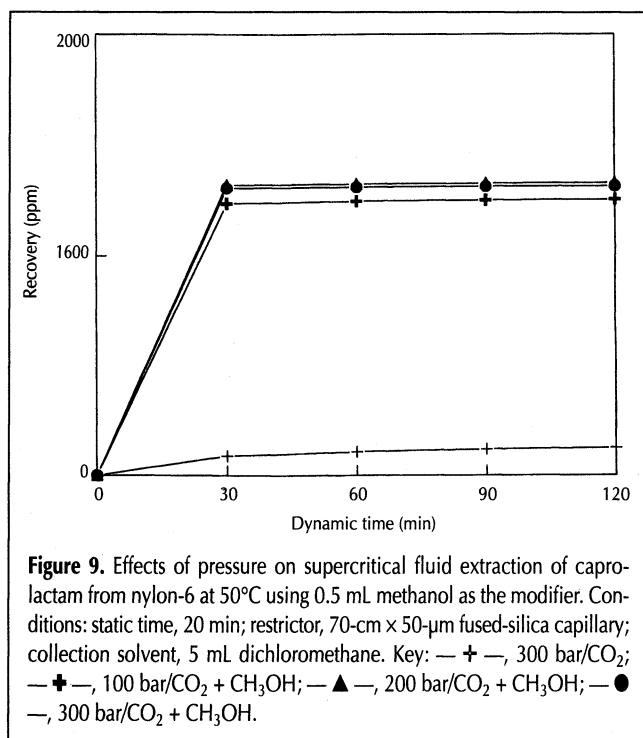
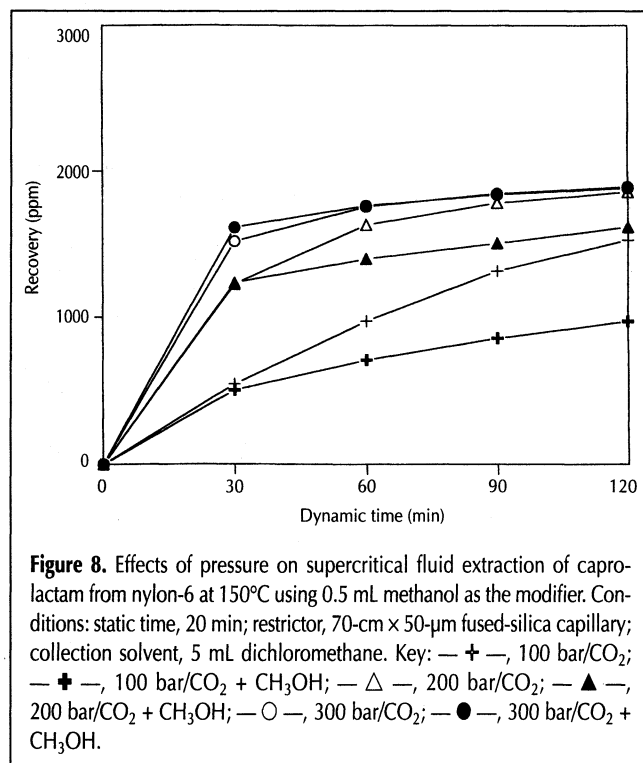


served for the extraction of the trimer from PBT. Here, the temperature at which the highest recovery was obtained in 2 h was 110°C, which was significantly lower than that for the dimer (150°C). In the results just discussed, extraction recoveries in 2 h were compared at different temperatures. The highest yield was obtained at 150°C for the dimer and at 110°C for the less soluble trimer.

It is also interesting to compare the total extraction recoveries in 2 h with the recoveries in the first half-hour fraction. The highest extraction recovery in the first half hour was obtained at 110°C for the dimer and at 90°C for the trimer. For both the dimer and the trimer, the temperatures at which the highest recoveries could be obtained in the first half-hour fractions were significantly lower than those in the total 2 h. Apparently, the influence of temperature on the extraction recovery can also be a function of analyte concentration. In the



beginning of the extraction, the concentration of the analytes on the surface of the polymer particles is relatively high. Hence, the solubility in the supercritical fluid is more likely to determine the extraction rate. During the extraction the concentration of the analytes gradually decreases. At lower concentrations the solubility of the analytes in the extractant becomes less critical. In addition to temperature, the extraction rates can also be greatly influenced by the addition of modifiers, as will be demonstrated.



Effects of modifiers

Influences of modifier identity and extraction temperature

In addition to temperature, the use of a modifier can also result in faster SFE of polymeric samples. The effects of different modifiers on the extraction efficiencies in the first half-hour fraction observed for the extraction of caprolactam from nylon-6 and the dimer and trimer from PBT at different temperatures are shown in Figures 4 and 5, respectively. Figure 6 shows the effects of modifier addition on the total extraction yields in 2 h. In these experiments, 0.5 mL of modifier was spiked to the extraction cell before extraction. The extraction recoveries with pure carbon dioxide are also shown in the figures for comparison. The highest temperature tested with modifiers for both polymers was 150°C. At higher temperatures, restrictor blocking was frequently observed. From these figures a number of interesting conclusions can be drawn:

- The influence of modifiers on the SFE of polymeric materials is significantly different with different modifiers.
- The effects of modifiers in the extraction of polymeric materials are strongly matrix-dependent. Among the four organic solvents tested, methanol is the most effective modifier for the extraction of nylon-6, whereas chloroform is preferred for the extraction of PBT.
- Modifiers are more effective at low temperatures.
- No abrupt changes in extraction efficiencies were observed around the normal glass transition temperatures of the polymers irrespective of which modifier was used. Modifiers are still very effective at temperatures below the normal polymer glass transition temperature.
- The influence of temperature on SFE is different when different modifiers are used.
- At high temperatures, modifiers can show negative effects on the extraction efficiency in the fractions after the first half hour. In the first half-hour fraction at 150°C and 300

bar, slight increases in the extraction recovery for caprolactam from nylon-6 and for the dimer from PBT as well as a larger increase for the less soluble trimer from PBT were observed when modifiers were added. However, the amounts extracted in later fractions for all analytes were considerably less than the amounts extracted in the corresponding fraction with pure carbon dioxide. This is especially true for the extraction of the dimer from PBT, in which the extraction recovery in 2 h with a modifier was significantly less than that with pure carbon dioxide.

The last phenomenon is surprising because modifiers are generally expected to always increase the extraction efficiency in SFE, as reported for the extraction of environmental samples (1,2,23). A possible reason for this is that when the modifier is "extracted" from the swollen polymer particles the particles will shrink, and changes in the structure of the polymer particles may occur, resulting in a more "closed" structure. These changes in structure can considerably slow down diffusion of the analytes out of the polymer particles. This occurs especially at high temperatures and when good swelling agents are used as modifiers.

From the results discussed above, it is clear that both optimization of temperature and of modifier identity are important in the extraction of polymeric materials. For the extraction of caprolactam from nylon-6 and the dimer from PBT, the greatest extraction yields that can be obtained by the variation of extraction temperature or by the addition of a modifier are of a similar magnitude. However, for the less soluble trimer, the addition of a modifier is more effective than the variation of temperature (Figure 6).

Effects of the modifier at diffusion and solubility-limiting conditions

The effects of modifiers on the extraction rate can be different depending on which parameter governs the extraction rate (i.e., diffusion or solubility). To investigate the modifier effects in more detail, polymeric samples were extracted with 0.5 mL of modifier (methanol for nylon-6 and chloroform for PBT) at different pressures and at temperatures of 50°C and 150°C. The results are shown in Figures 7–10. At conditions for which solubility is the rate-limiting parameter (e.g., at 150°C with

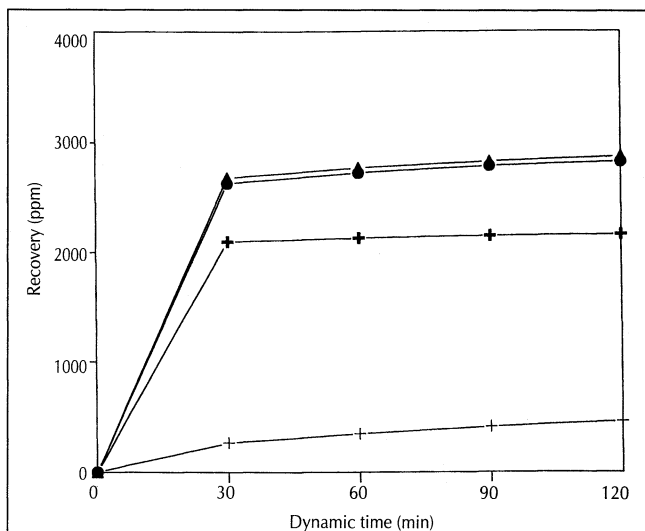


Figure 10. Effects of pressure on supercritical fluid extraction of the dimer from PBT at 50°C using 0.5 mL chloroform as the modifier. Conditions: static time, 20 min; restrictor, 70-cm \times 50- μ m fused-silica capillary; collection solvent, 5 mL dichloromethane. Key: — + —, 300 bar/CO₂; — + —, 100 bar/CO₂ + CHCl₃; — \blacktriangle —, 200 bar/CO₂ + CHCl₃; — \bullet —, 300 bar/CO₂ + CHCl₃.

Table I. Effects of Modifier Amount on the Supercritical Fluid Extraction Yield in the First Half-Hour Fraction at 50°C and 300 bar*

Modifier amount (mL)	Polymer/Analyte		
	Nylon-6/Caprolactam (ppm) [†]	PBT [†] /Dimer (ppm) [‡]	PBT/Trimer (ppm) [‡]
0	89.5	268.0	27.8
0.2	883.5	1238.9	264.5
0.5	1308.4	2629.3	683.1
0.8	1574.2	3577.2	1051.9

* Static time, 20 min; dynamic time, 30 min.

[†] PBT = poly(1,4-butylene terephthalate).

[‡] Extracted amount relative to the mass of polymer weighed into the extraction cell.

pure carbon dioxide), the extraction recoveries for all analytes increased significantly at increased pressures (Figures 7 and 8). Besides pressure, modifiers can also improve the density and polarity of the supercritical fluid, thus increasing the solubility. In the extraction of PBT with 0.5 mL chloroform as modifier, the extraction recovery of the first half-hour fraction for the dimer increased significantly at all pressures tested (Figure 7A). Even greater increases in the extraction recovery were observed for the less soluble trimer (Figure 7B). In contrast, no significant increase in the extraction recovery in the first half-hour fraction was observed for the extraction of caprolactam from nylon-6 when 0.5 mL methanol was added as the modifier (Figure 8). Even more surprising is the observation that modifiers can also have negative effects at low pressures (100 and 200 bar) in the extraction of caprolactam from nylon-6. Similar negative effects of the modifier were also observed in the extraction of the dimer from PBT. From Figures 7 and 8, it can also be seen that the extraction recovery found at 150°C using 0.5 mL methanol and 0.5 mL chloroform as modifiers increased significantly at increased pressures. This means that at this temperature the improvement of the solubility by the addition of modifier directly into the extraction cell is not sufficient. The extraction rate is still limited by the solubility of the analytes in the supercritical fluid.

Also, at conditions for which diffusion in the polymer is the rate-limiting parameter, the addition of modifier can be very attractive. To investigate the effects of modifiers on diffusion in the polymer, a series of extractions with modified carbon dioxide was performed at different pressures and a temperature of 50°C. As discussed before, no considerable variations in extraction recovery of the analytes from both polymers were observed at 50°C when the extraction pressure was increased from 150 to 300 bar and pure carbon dioxide was used. This indicates that at these conditions the rate-limiting parameter is diffusion in the polymer. Suitable modifiers can swell the polymer, thereby increasing diffusion of the analytes in the polymer. Much greater recoveries were observed for both polymers with modified carbon dioxide relative to those with pure carbon dioxide at all pressures tested. Figures 9 and 10 show the effects of pressure on SFE of caprolactam from nylon-6 and the dimer from PBT. Similar effects were also observed for the

trimer. With modified carbon dioxide, the extraction recoveries are already fairly large at 100 bar. Only slight increases of recoveries were observed when the extraction pressure was increased from 100 to 200 bar. A further increase in pressure gave no further improvement in extraction recovery. This is probably because the density of the modified supercritical fluid is already high even at pressures as low as 100 bar. As the solubility of the components in the supercritical fluid is large, the rate-limiting parameter at 50°C with modified carbon dioxide is diffusion of the analytes in the polymer particles.

To investigate the contribution of the modifier to the overall extraction, a series of experiments was performed in which the same modifier was used but carbon dioxide was replaced by helium. When the experiments described above were repeated using helium (150 bar) as the carrier medium instead of supercritical carbon dioxide, only a small amount of caprolactam and no dimer or trimer could be extracted. It is clear from these results that the extracting capability of the modified supercritical fluid is not simply the addition of that of the pure supercritical carbon dioxide and of the neat modifier.

Influence of modifier concentration, static time, and supercritical fluid flow rate

From the preceding paragraphs it can be seen that the effects of a modifier are (a) swelling of the polymer particles, thereby enhancing diffusion of analytes inside the particles; and (b) increasing the solvent strength of the supercritical extractant. The relative extent of these two effects is determined not only by the modifier identity and its concentration but also by its residence time in the extraction cell (if modifiers are spiked onto the sample). The effects of different amounts of modifier on the extraction recoveries are listed in Tables I and II. These experiments were performed at 300 bar and temperatures of 50°C and 150°C. The largest amount of modifier added directly into the extraction cell was 0.8 mL. Larger amounts could not be accommodated by the polymer and leaked out of the extraction cell immediately. As was expected, the extraction recoveries increased considerably at greater modifier concentrations.

In our experiments modifiers were added directly into the extraction cell. The contact time of the modifier and the matrix depends on the static time, the modifier amount and identity, matrix properties, the extraction temperature and pressure, and supercritical fluid flow rate. At 50°C and 300 bar, the amounts

Table II. Effects of Modifier Amount on the Supercritical Fluid Extraction Yield in the First Half-Hour Fraction at 150°C and 300 bar*

Modifier amount (mL)	Polymer/Analyte		
	Nylon-6/Caprolactam (ppm) [‡]	PBT [†] /Dimer (ppm) [‡]	PBT/Trimer (ppm) [‡]
0	1518.7	1110.2	47.4
0.2	1525.4	1319.0	84.8
0.5	1614.5	1977.2	484.9
0.8	NT [§]	2793.8	1203.0

* Static time, 20 min; dynamic time, 30 min.

[†] PBT = poly(1,4-butylene terephthalate).

[‡] Extracted amount relative to the mass of polymer weighed into the extraction cell.

[§] Not tested.

Table III. Effects of Static Time on the Supercritical Fluid Extraction Yield in the First Half-Hour Fraction at 50°C and 300 bar*

Static time (min)	Polymer/Analyte		
	Nylon-6/Caprolactam (ppm) [‡]	PBT [†] /Dimer (ppm) [‡]	PBT/Trimer (ppm) [‡]
10	1264.2	2400.5	589.9
20	1308.4	2629.3	683.1
30	1433.6	2989.0	787.5

* Dynamic time, 30 min.

[†] PBT = poly(1,4-butylene terephthalate).

[‡] Extracted amount relative to the mass of polymer weighed into the extraction cell.

extracted in the first half-hour fraction increased continuously when the static time was increased from 10 to 30 min (Table III). In contrast to this, no considerable changes in extraction recovery with different static times were observed at 150°C and 300 bar. At 50°C and 300 bar the effects of the modifier result mainly from swelling of the polymer. Normally, swelling is a slow process, which means that longer static times can be of benefit. On the other hand, the main effect of modifiers at 150°C and 300 bar is to increase the solvent strength of the supercritical fluid. Therefore, the extraction recovery at 150°C and 300 bar will not change considerably with increasing static time.

In the experiments described above, a piece of fused-silica capillary (70 cm × 50- μ m i.d.) was used as the flow restrictor. To investigate the effects of the supercritical fluid flow rate on the extraction recovery of the analytes, this restrictor was replaced by 20- μ m i.d. fused-silica capillaries with lengths of 70 cm and 20 cm. The effects of the fluid flow rates on the extraction recoveries of both polymers at 50°C and 300 bar are listed in Table IV. In these experiments 0.5 mL of modifier was used. At 150°C the effects of fluid flow rate could not be tested because at these conditions the 20- μ m i.d. fused-silica restrictor became easily blocked. The extraction recoveries in the first half-hour fraction increased considerably when the supercritical fluid flow rate was decreased from 550 (gas flow measured at ambient conditions) to 110 mL/min. However, no further increase in the extraction recovery was observed when the flow rate was further decreased from 110 to 35 mL/min. Nevertheless, the total extraction recovery obtained in 2 h still increased slightly in this case. Because the trapping efficiency is quantitative even at the highest supercritical fluid flow rate tested, the increased extraction recoveries must be due to the longer contact time of the modifier with the polymeric matrix at lower supercritical fluid flow rates. It is clear from these data that the extraction recovery is a function of the extractant volume swept through the extraction cell, as well as of the contact time of the modifier with the matrix. Maximizing the contact time by either continuous addition of a modifier or repeated spiking is advantageous, as will be demonstrated.

Introduction of an additional amount of modifier through an LC injection valve

From the results described above, it can be seen that the kinetics of SFE of polymeric materials are complex. Optimiza-

tion of the extraction conditions should at least include the selection of the proper extraction temperature and modifier type and concentration. Modifiers are more effective at low temperatures and at higher concentrations. However, the modifier amount that can be added is limited if the modifiers are spiked directly into the extraction cell. To be able to introduce larger amounts of modifier, an LC injection valve was installed before the extraction cell. In this series of experiment, only the amounts extracted in the first half-hour fractions were investigated. Flow restriction was provided by a piece of fused-silica capillary (20 cm × 20- μ m i.d.). The results are listed in Table V. It can be seen from this table that if 0.8 mL of modifier is added directly to the extraction cell before extraction, after which 2.0 mL is introduced through the injection valve, the SFE recoveries of caprolactam from nylon-6 and the dimer from PBT in 30 min are already almost identical to those found for Soxhlet extraction with methanol or chloroform in 30 h. However, the recovery for the less soluble trimer from PBT in 30 min is still considerably lower than that of Soxhlet extraction with chloroform in 30 h. In the SFE of less soluble and larger solutes from polymeric samples, continuous modifier addition is likely to be more effective. This will be the subject of future investigations.

Conclusions

The extraction rate in SFE of polymeric samples is governed by either diffusion of the solutes in the polymer particles or their solubility in the extraction fluid. If the rate-limiting parameter is diffusion of the analytes in the polymer particles, increasing extraction temperature will increase the extraction rate. On the other hand, if the rate-limiting parameter is solubility of the analytes in the supercritical extractant, increasing temperature will have an adverse effect on extraction yields. In addition to variation of temperature, the addition of modifiers can also strongly affect the extraction rate for SFE. Our results suggest that the role of modifier in the extraction of polymeric samples is twofold. A suitable modifier increases the solvent strength of the supercritical fluid and swells the polymer particles, which results in enhanced diffusion in the polymer. Both modifier identity and concentration were found to be important

Table IV. Effects of Supercritical Fluid Flow Rate on the Supercritical Fluid Extraction Yield in the First Half-Hour Fraction at 50°C and 300 bar*

Flow rate (mL/min)	Polymer/Analyte		
	Nylon-6/Caprolactam (ppm) [†]	PBT [†] /Dimer (ppm) [‡]	PBT/Trimer (ppm) [‡]
550	1308.4	2629.3	683.1
110	1420.2	2850.8	771.8
35	1429.6	2898.7	771.3

* Static time, 20 min; dynamic time, 30 min; modifier, methanol (nylon-6) and chloroform (PBT).
[†] PBT = poly(1,4-butylene terephthalate).
[‡] Extracted amount relative to the mass of polymer weighed into the extraction cell.

Table V. Comparison of Recoveries Obtained in Supercritical Fluid Extraction (SFE) and Soxhlet Extraction

Extraction method	Polymer/Analyte*		
	Nylon-6/Caprolactam (ppm)	PBT [†] /Dimer (ppm)	PBT/Trimer (ppm)
SFE [‡]	1816.8	4810.8	1484.7
Soxhlet	1827.8	4886.0	2039.0

* Extracted amount relative to the mass of polymer weighed into the extraction cell.
[†] PBT = poly(1,4-butylene terephthalate).
[‡] Temperature, 50°C; pressure, 300 bar; static time, 20 min; dynamic time, 30 min; modifier, methanol (nylon-6) and chloroform (PBT).

for increasing the extraction efficiency. Modifiers are generally more effective at low temperatures. At high temperatures, modifiers may sometimes even have negative effects on the extraction efficiency. Also, the contact time between the modifier and the matrix is of importance. Continuous modifier addition or repeated spiking of a modifier may be advantageous if spiked modifiers are eluted rapidly or if higher modifier concentrations are needed.

References

1. S.B. Hawthorne. Analytical-scale supercritical fluid extraction. *Anal. Chem.* **62**: 633A–42A (1990).
2. T.L. Chester, J.D. Pinkston, and D.E. Raynie. Supercritical fluid chromatography and extraction. *Anal. Chem.* **66**: 106R–30R (1994).
3. *Analytical Supercritical Fluid Chromatography and Extraction*. M.L. Lee and K.E. Markides, Eds. Chromatography Conference, Provo, UT, 1990.
4. J.G.M. Janssen, P.J. Schoenmakers, and C.A. Cramers. A fundamental study of the effects of modifiers in supercritical fluid chromatography. *J. High Resolut. Chromatogr.* **12**: 645–51 (1989).
5. J.M. Levy, L. Dolata, R.M. Ravey, E. Storzynsky, and H.A. Holowczak. Use of modifiers in on-line and off-line supercritical fluid extraction. *J. High Resolut. Chromatogr.* **16**: 368–71 (1993).
6. T.M. Fahmy, M.E. Paulaitis, D.M. Johnson, and M.E.P. McNally. Modifier effects in the supercritical fluid extraction of solutes from clay, soil, and plant materials. *Anal. Chem.* **65**: 1462–69 (1993).
7. J. Dankers, M. Groeneboom, L.H.A. Scholtis, and C. van de Heiden. High-speed supercritical fluid extraction method for routine measurement of polycyclic aromatic hydrocarbons in environmental soils with dichloromethane as a static modifier. *J. Chromatogr.* **641**: 375–62 (1993).
8. T.S. Oostdyk, R.L. Grob, J.L. Snyder, and M.E. McNally. Optimization of the supercritical fluid extraction of primary aromatic amines. *J. Chromatogr. Sci.* **31**: 177–82 (1993).
9. J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, and J. Pawliszyn. Role of modifiers for analytical-scale supercritical fluid extraction of environmental samples. *Anal. Chem.* **66**: 909–16 (1994).
10. Y. Lin and C.M. Wai. Supercritical fluid extraction of lanthanides with fluorinated b-diketones and tributyl phosphate. *Anal. Chem.* **66**: 1971–75 (1994).
11. K.E. Laintz and E. Tachikawa. Extraction of lanthanides from acidic solutions using tributyl phosphate modified carbon dioxide. *Anal. Chem.* **66**: 2190–93 (1994).
12. J.W. Hills, H.H. Hill, D.R. Hansen, and S.G. Metcalf. Carbon dioxide supercritical fluid extraction of incinerator fly ash with a reactive solvent modifier. *J. Chromatogr.* **679**: 319–28 (1994).
13. B.E. Berg, E.M. Hansen, S. Gjørven, and T. Greibrokk. On-line enzymatic reaction, extraction, and chromatography of fatty acids and triglycerides with supercritical carbon dioxide. *J. High Resolut. Chromatogr.* **16**: 358–63 (1993).
14. X. Lou, H.-G. Janssen, and C.A. Cramers. Investigation of parameters affecting the supercritical fluid extraction of polymer additives from polyethylene. *J. Microcol. Sep.* **7**: 303–17 (1995).
15. A. Venema, H.J.F.M. van de Ven, F. David, and P. Sandra. Supercritical fluid extraction of nylon-6: an investigation into the factors affecting the efficiency of extraction of caprolactam and its oligomers. *J. High Resolut. Chromatogr.* **16**: 522–24 (1993).
16. K.D. Bartle, A.A. Clifford, S.B. Hawthorne, J.J. Langenfeld, D.J. Miller, and R. Robinson. A model for dynamic extraction using a supercritical fluid. *J. Supercrit. Fluids* **3**: 143–49 (1990).
17. N.J. Cotton, K.D. Bartle, A.A. Clifford, and C.J. Dowle. Rate and extent of supercritical fluid extraction of cyclic trimer from poly(ethylene terephthalate) at elevated temperatures. *J. Chromatogr. Sci.* **31**: 157–61 (1993).
18. S. Kueppers. The use of temperature variation in supercritical fluid extraction of polymers for the selective extraction of low molecular weight components from poly(ethylene terephthalate). *Chromatographia* **33**: 434–40 (1992).
19. J.C. Via, C.L. Braue, and L.T. Taylor. Supercritical fluid fractionation of a low molecular weight, high-density polyethylene wax using carbon dioxide, propane, and propane-modified carbon dioxide. *Anal. Chem.* **66**: 603–609 (1994).
20. J.A. Pratt, S.H. Lee, and M.A. McHugh. Supercritical fluid fractionation of copolymers based on chemical composition and molecular weight. *J. Appl. Polym. Sci.* **49**: 953–66 (1993).
21. Y. Yang, A. Gharaibeh, S.B. Hawthorne, and D.J. Miller. Combined temperature/modifier effects on supercritical CO₂ extraction efficiencies of polycyclic aromatic hydrocarbons from environmental samples. *Anal. Chem.* **67**: 641–46 (1995).
22. R.A. Orwell. Solubility of polymers. In *Encyclopedia of Polymer Science and Engineering*, vol. 15. H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges, and J.I. Kroschwitz, Eds. John Wiley & Sons, New York, NY 1989, p 380.
23. M.E.P. McNally. Advances in environmental SFE. *Anal. Chem.* **67**: 308A–15A (1995).

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