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Effect of Thermal Annealing and Supercritical Fluids on the Crystallization Behavior of Methyl-Substituted Poly(aryl ether ether ketone)†

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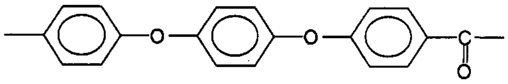
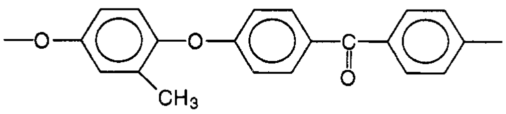
ABSTRACT: The glass transition temperature of MePEEK, a monosubstituted methyl derivative of poly(aryl ether ether ketone), PEEK, is 145 °C, the same as that of PEEK. However, the onset of melting of MePEEK, crystallized by thermal annealing, occurs at 210 °C, much lower than the onset at 335 °C observed for PEEK. MePEEK, crystallized by successively annealing for 100 min each at 175, 190, and 200 °C, melts in a two-step process spread over a broad temperature range of about 50 deg. This double melting behavior is observed in PEEK also. When MePEEK is annealed in a similar manner in the presence of supercritical CO_2 at 100 atm, the melting event is still broad but the two peaks are now overlapped. Similar conditioning in the presence of supercritical $0.9CO_2 + 0.1CH_2Cl_2$ and $0.9CO_2 + 0.1CH_3OH$ at 100 atm gives a single and sharp melting peak with onset at 229 and 260 °C, respectively. The melting event is now spread over about 15 deg only. The density of amorphous MePEEK is 1.233 g cm^{-3}. The density and heat of melting of 100% crystalline MePEEK are estimated to be 1.348 g cm^{-3} and 74 J g^{-1}, respectively, on the basis of density, thermal, and X-ray diffraction measurements on semicrystalline samples. The corresponding values for PEEK are 1.40 g cm^{-3} and 130 J g^{-1}.

Introduction

Poly(aryl ether ether ketone) is a high-performance thermoplastic of considerable commercial interest. As a result, numerous studies on its thermal[1,2] and morphological[1,3–7] characteristics and crystallization[1,3,4,8] behavior have been reported. On heating the amorphous sample from room temperature,[9] PEEK undergoes a glass transition at about 145 °C and a spontaneous and sharp crystallization transition at about 170 °C which induces a crystallinity of about 16% in the sample. The extent of crystallinity continues to increase with temperature and reaches about 34% just before the onset of melting at about 335 °C. The melting transition is usually a single, broad peak. However, if the sample is annealed at a temperature between the crystallization and the melting temperatures,[2,4,10] then the melting event shows two peaks; the first peak occurs at a temperature about 10–15 deg above the annealing temperature, and the second peak, at or slightly above the original melting point. Thus, depending on the annealing temperature, the two melting peaks are either well-separated or overlapped. Nevertheless, the melting peaks remain relatively broad. If the sample is annealed just below the melting point,[4,11] a single and sharp melting peak is observed. On the other hand, if the sample is annealed above the original melting point, then, again, two melting peaks are observed; a broad low temperature peak and a smaller but sharper high-temperature peak. The origin of the double melting in PEEK has been attributed[4,6,7] to the existence of two crystalline populations; thinner lamellar morphologies which grow between the thicker lamellae. The origin of the single, sharp melting peak has been attributed to the self-seeding crystallization[4] whereby the polymer melts and recrystallizes at 330 °C, leading to more perfect crystals. The repeat unit of PEEK has the structure



Recently, we reported[12] the synthesis of methyl-substituted PEEK (MePEEK) where the repeat unit has the following structure



and every ether–phenylene–ether unit in the polymer is substituted with one methyl group. The structural, viscoelastic, and some basic thermal properties of MePEEK were also reported.[12] The glass transition temperature of MePEEK is 145 °C, the same as that of PEEK. However, unlike PEEK, MePEEK does not undergo spontaneous crystallization. Instead, crystallinity can be induced only if MePEEK is annealed at a temperature between 175 and 200 °C. The onset of the melting point for MePEEK was found to be 210 °C, much lower than that of PEEK. However, the melting event did show a broad doublet, as observed in the case of thermally annealed PEEK. The purpose of the present paper is to explore further the crystallization behavior of MePEEK.

Thermal annealing allows the polymer to lose its excess free energy and develop some long range order due to the fast relaxation times available above the glass transition temperature, T_g. Similar relaxation times become accessible when a polymer is plasticized due to sorption of vapors or liquids at temperatures much below T_g, thus leading to crystallization of the polymer below the bulk T_g. This vapor-[13] or liquid-induced[14,15] crystallization has been studied in the case of PEEK. It is now well-established[9] that compressed gases or supercritical fluids can also plasticize the polymers, leading to a depression in T_g to almost the same extent as effected by vapors or liquids. There are a few advantages of using supercritical fluids over vapors or liquids. The thermodynamic activity of a vapor is limited by its saturation vapor pressure, and that

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of a liquid, by its solubility in the polymer. On the other hand, the activity of a supercritical fluid can be continuously changed by simply changing its pressure. This provides a highly tunable technique to change the morphology or crystallinity in a controlled manner. There are a few limits. At much higher pressures, the solubility of the supercritical fluid in the polymer reaches its limiting value due to the hydrostatic pressure exerted by the fluid,[16,17] and at temperatures close to the critical temperature of the fluid, rather complex phase behavior is encountered.[18,19] Nevertheless, there is usually available a wide temperature–pressure window within which the supercritical fluid can act as an efficient plasticizer. Furthermore, after bringing about the desired morphological change, the fluid is easily removed from the polymer matrix by simply depressurizing the system whereas sorbed vapors or liquids do not desorb as easily.

Since supercritical fluids can lower the T_g by several tens of degrees,[9] it implies that they will also lower the crystallization temperature. This indeed was found to be the case for the PEEK–CO_2 system[9] where crystallinity was induced at temperatures as low as 100 °C. That supercritical fluids can induce crystallinity in polymers was first recognized by Chiou *et al.*[20] in their study of the poly(vinylidene fluoride)–CO_2 system. Similar investigations have been reported for poly(ethylene terephthalate),[20-22] Bisphenol A polycarbonate,[23] and poly(phenylene sulfide)[24,25] with CO_2 and for PPS[25] with N_2O. In general, these studies show that supercritical fluids can induce crystallinity below T_g and crystallization rate increases with temperature and pressure, and levels of crystallinity comparable to those induced by organic liquids are easily achieved.

As noted above, MePEEK does not undergo crystallization easily and, for the molecular weight range studied,[12] was found to have a rather narrow temperature range available over which crystallinity could be induced by thermal annealing. This makes it an ideal candidate to study its crystallization behavior by other means. To this end, we have examined the crystallization of MePEEK with various supercritical fluids and under various thermal treatments. This work is reported here.

Experimental Section

The MePEEK used was from the batch FW59B2 whose characteristics we reported previously.[12] The M_w of the sample was 23 800, and M_w/M_n was 1.27. Fluids used were sfc-grade CO_2, $0.9CO_2 + 0.1CH_2Cl_2$, and $0.9CO_2 + 0.1CH_3OH$, all obtained from Scott Specialty Gases.

Density measurements were made using the helium pycnometer (Micromeritics, Model AccuPyc 1330). The reproducibility of the measurements was ±0.003 g cm^{-3}. Thermal analysis was done using a DSC2910 (TA Instruments). All scans were made at 10 °C min^{-1} under a dry nitrogen gas flow rate of 50 mL min^{-1}. Calibrations of the temperature and energy scales of the DSC have been described previously.[26] X-ray diffraction patterns were collected at room temperature using a Scintag diffractometer (Model XDS 2000) equipped with a graphite monochromator and a Cu Kα radiation source.

The polymer samples were treated with supercritical fluids using a supercritical fluid extraction-supercritical fluid chromatography instrument (Suprex, Model MPS/225). Calibrations of the temperature and pressure scales of the Suprex machine were checked using a platinum resistance thermometer (Omega, Model 651) and a Setra pressure transducer (Model 204), respectively. About a 1 m long loop of 1.59 mm internal diameter tube, connecting the pump and the extraction vessel, was installed in the oven. This ensured that the compressed liquid delivered by the pump reached the supercritical state and equilibrated to the oven temperature before entering the extraction vessel. An appropriate amount of the polymer sample was loaded in a 5 mL extraction vessel, the oven was quickly brought to the required temperature, and the sample was contacted with the supercritical fluid at the desired pressure. The samples were treated in the temperature range 100–200 °C, at pressures from 100 to 300 atm, and for times ranging from a few minutes to 100 min. After treatment with the fluid, the pressure was slowly reduced to ambient, the extraction vessel was allowed to cool to room temperature, and the sample was removed from the extraction vessel. The critical temperature of CO_2 is 31.2 °C. The critical temperatures of both binary fluids were estimated to be about the same, 54 °C, using the theory of corresponding states.[27] Thus, at no stage during the treatment process did the samples come in contact with the condensed phase of the fluid. The recovered samples were kept under vacuum overnight in order to remove any residual gas.

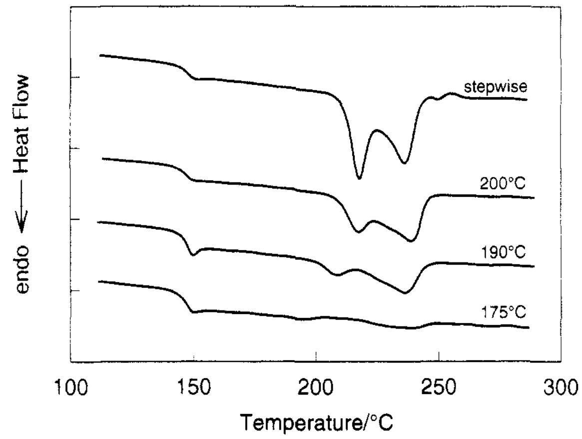

Figure 1. Melting behavior of MePEEK crystallized by annealing for 100 min at the temperatures indicated. Stepwise annealing pertains to successively annealing for 100 min each at 175 °C, then at 190 °C, and then at 200 °C.

A few samples were annealed thermally only, in the absence of any fluid. These samples were prepared either in the DSC sample pan or in the Suprex extraction vessel. In either case, after annealing for the required time, the samples were allowed to cool back to room temperature before conducting any DSC measurements. A nominal sample mass used for DSC analysis was about 8 mg and for density measurements was about 40 mg.

Results and Discussion

The DSC results are shown in Figures 1–7. The heat flow signal in all the scans is normalized to the unit mass of the sample. In each figure, the scans have been shifted vertically for the sake of clarity. The curves labeled *stepwise* refer to the samples where the annealing temperature was successively increased from 175 to 190 °C and then to 200 °C, keeping the sample at each temperature for 100 min.

The DSC scans for the samples annealed thermally only are shown in Figure 1. All samples were annealed for 100 min at the temperatures indicated. In all cases, a glass transition is seen at about 145 °C. Only a trace amount of crystallinity was observed in the samples (not shown in Figure 1) annealed at 150 °C for 100 min and 175 °C for 30 min. However, for the results shown in Figure 1 at 175 °C, two melting events can clearly be identified with peak maxima at about 190 and 240 °C. As the annealing temperature is raised, the melting peaks grow in amplitude and the first peak moves to higher temperatures whereas the temperature of the second peak remains almost the same. As a result, the two melting events, well-separated at the lower temperature, get progressively closer and, eventually, a doublet is seen for the *stepwise* sample. The latter result is similar to the one reported earlier,[12] and the double melting behavior is reminiscent of the well-established double melting of PEEK.

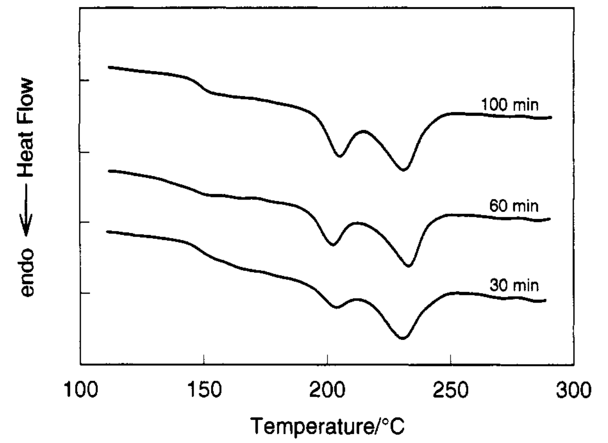

Figure 2. Melting behavior of MePEEK crystallized at 175 °C by contacting with supercritical CO_2 at 100 atm for the times indicated.

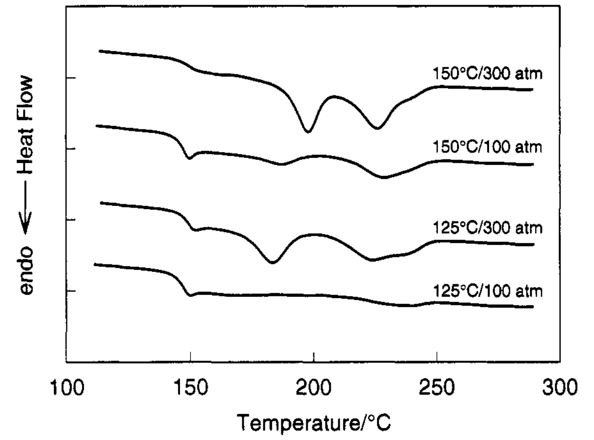

Figure 3. Melting behavior of MePEEK crystallized by contacting with supercritical CO_2 for 100 min at the temperatures and pressures indicated.

The scans for the samples annealed at 175 °C in the presence of CO_2 at 100 atm are shown in Figure 2. In this case, the crystallinity is well-developed after 30 min of treatment, as compared to the sample which was only thermally treated at 175 °C, Figure 1. There is a slight increase in the area of the melting peaks when the CO_2 treatment time is increased from 30 to 60 min but almost no change in going from 60 to 100 min. Consequently, the annealing time was chosen as 100 min in all the cases studied. The effects of temperature and pressure on treatment with CO_2 are shown in Figure 3. A trace amount of crystallinity is induced at 125 °C and 100 atm that increases significantly on increasing the pressure to 300 atm. The crystallinities induced at 150 °C and 100 and 300 atm are higher than the corresponding effects at 125 °C. For the samples treated at 300 atm, a third melting peak is seen as a small shoulder at the high-temperature end. For the rest of the measurements, a pressure of 100 atm was used; the effect of using higher pressures is currently being studied in detail. The results in Figures 2 and 3 clearly establish that supercritical CO_2, due to its plasticizing effect, can induce crystallinity below the glass transition temperature of the polymer and that higher levels of crystallinity are obtained when compared to samples annealed thermally only at the corresponding temperatures. The effect of temperature on treatment with CO_2 at 100 atm is shown in further detail in Figure 4. As in the case with thermal treatment alone, Figure 1, the effect of increasing the temperature is to shift the first melting peak to progressively higher temperatures and to increase its amplitude. The increasing temperature brings the two peaks closer, and for the *stepwise* case, the first melting event gives a well-defined peak and the second melting event appears as a shoulder. However, the overall melting event still covers a relatively broad temperature range of about 40 deg. PEEK, on the other hand, gave[9] a single but broad melting peak when crystallized with CO_2 at 100 °C. However, in PEEK, it is not possible to distinguish between the crystallinity induced by CO_2 and that induced, at its crystallization temperature of 175 °C, during the DSC scan; in fact, the CO_2-induced crystals may act as seeds for the spontaneous crystallization at 175 °C. Thus, a direct comparison between the melting behaviors of supercritical fluid-crystallized PEEK and MePEEK is not possible on the basis of DSC measurements alone.

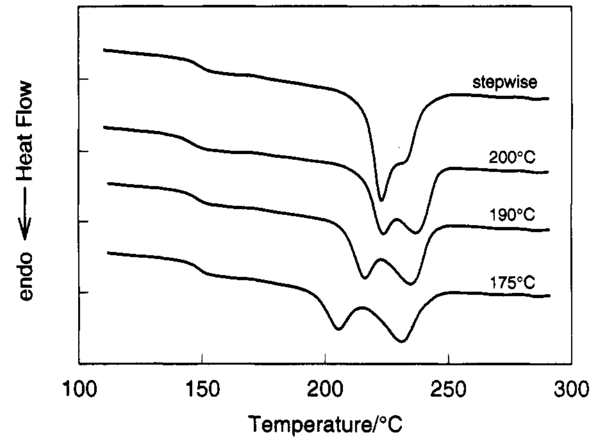

Figure 4. Melting behavior of MePEEK crystallized by contacting with supercritical CO_2 at 100 atm for 100 min at the temperatures indicated. Stepwise treatment pertains to successively contacting with the supercritical fluid at 100 atm for 100 min each at 175 °C, then at 190 °C, and finally at 200 °C.

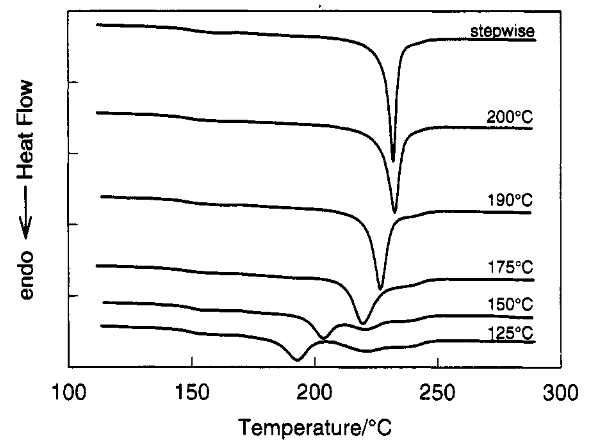

Figure 5. Melting behavior of MePEEK crystallized by contacting for 100 min with supercritical CO_2 + 10% CH_2Cl_2 at 100 atm at the temperatures indicated. Stepwise treament was the same as in Figure 4.

MePeek is soluble in CH_2Cl_2. A 5% by mass solution was prepared, the solvent was then evaporated, and the residual MePEEK was scanned. The sample was found to have crystallized, and it melted with a single, broad peak at 210 °C. Figure 5 shows scans on the samples treated with the supercritical fluid CO_2 + CH_2Cl_2 at 100 atm at the temperatures indicated. The presence of CH_2Cl_2 helps the sample to develop a significant amount of crystallinity at 125 °C whereas, as seen in Figure 4, only a trace amount of crystallinity was detected at 125 °C using CO_2 alone. Another observation of note is that as the annealing temperature is increased, the two melting peaks merge to give a single, broad peak at 175 °C. With

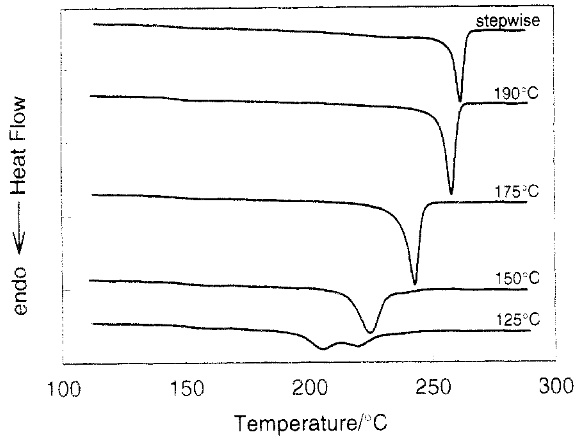

Figure 6. Melting behavior of MePEEK crystallized by contacting for 100 min with supercritical CO_2 + 10% CH_3OH at 100 atm at the temperatures indicated. Stepwise treatment was the same as in Figure 4.

a further increase in temperature, this peak sharpens considerably and finally the *stepwise* treatment gives a single and unusually sharp melting peak. Such a sharp peak is often associated with melting of pure molecular solids; the semicrystalline polymers usually melt over a broad temperature range. Even more interesting are the results shown in Figure 6 for the samples treated with supercritical CO_2 + CH_3OH. With the present fluid, a single but broad melting peak is already obtained at 150 °C. At higher annealing temperatures, this peak not only sharpens but moves to higher temperatures also. The *stepwise* treatment again gives the most pronounced effect. MePEEK does not dissolve in CH_3OH. A sample was soaked in CH_3OH for 24 h, dried, and scanned. This sample did not show any crystallinity. Thus, whereas pure CH_3OH is ineffective in inducing any crystallinity, it becomes a very effective agent when used in the supercritical state. There is also a marked effect of the addition of a small amount of CH_2Cl_2 or CH_3OH to CO_2 on the extent of crystallinity induced. In Figures 1, 3, and 4, the area under the melting peak(s) increases rapidly with an increase in the annealing temperature. In the case of CO_2 + CH_2Cl_2, Figure 5, the peak area changes only by about 6% in going from 125 to 175 °C and then remains almost constant with higher temperature treatments. In the case of CO_2 + CH_3OH, Figure 6, the peak area is almost the same at all temperatures; only the shape of the melting peak changes.

The barrier to main-chain motion in a polymr can be overcome either by increasing its temperature or by dissolving enough diluent in it or by a combination of both factors. In the case of polymer–supercritical fluids, it is a subtle combination of both temperature and the solubility of the fluid which determines the plasticization of the polymer.[18] The effect of plasticization by the different fluids is seen in Figures 3, 5, and 6 in terms of crystallization of MePEEK below its bulk T_g. However, at temperatures above the T_g, the polymer is already plasticized in terms of the degrees of freedom available to the main chain. In fact, at 200 °C, the solubility of the fluid in the polymer is very small, and yet, the presence of a very small amount of CO_2, and especially CO_2 + a cosolvent, brings about dramatic effects in the melting behavior of MePEEK. The best-case scenarios for the various treatments are summarized in Figure 7 and refer to the *stepwise* treatments. For the curve labeled *thermal*, the sample was annealed in the absence of any fluid in the Suprex extraction vessel rather than in the DSC pan in order to provide it with the same thermal history as the other samples. The heats of melting, ΔH, for the various samples are summarized in Table 1. The extent of crystallinity does not change much with the treatment used, as indicated by the constancy of the ΔH values. For the four stepwise treatments shown, the onset of melting is at 210, 216, 229, and 258 °C and the temperature ranges over which melting is observed are 50, 40, 20, and 15 deg, respectively. Clearly, it is the nature of the crystallites produced that changes drastically with the use of the supercritical fluid, and the presence of a polar cosolvent in CO_2 produces crystals which undergo melting at higher temperatures and over a much narrower temperature range. The use of CH_3OH as a cosolvent produces crystals relatively more stable than those produced when CH_2Cl_2 is used as a cosolvent. This finding is particularly intriguing because, as noted above, pure liquid CH_3OH does not bring about any morphological change in MePEEK whereas pure liquid CH_2Cl_2 readily crystallizes it.

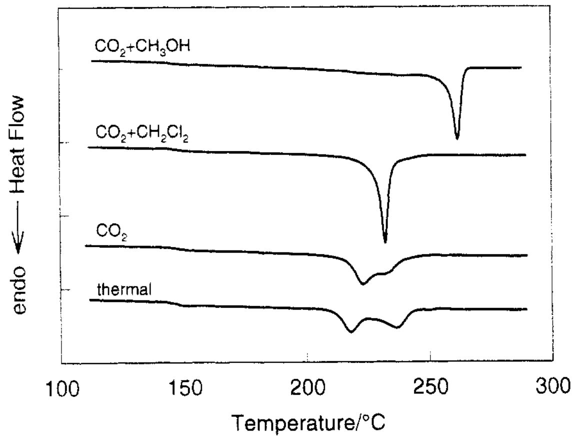

Figure 7. Comparison of the melting behaviors of MePEEK crystallized using the stepwise treatments reported in Figures 1 and 4–6.

Table 1. Density, Heat of Melting, and Crystallinity Values for MePEEK Samples Treated in the Stepwise Mode

treatment	ρ/(g cm^{-3})	ΔH/(J g^{-1})	% crystallinity
untreated	1.233	0	0
thermal	1.267	20.2	27
CO_2	1.260	20.2	25
CO_2 + CH_2Cl_2	1.257	19.6	27
CO_2 + CH_3OH	1.274	20.0	29

In an idealized DSC with a time constant of zero, a thermal event will give a signal with an instantaneous rise and decay and, thus, will appear as a spike. In an actual DSC with a finite time constant, the width of a transition peak depends on the mass of the sample, the scan rate, and the heat change associated with the thermal event. In the present work, all scans were made at the same rate and care was taken to use the same sample mass. Furthermore, as seen in Table 1, the heat of melting of the different samples in Figure 7 is almost the same and yet they give melting peaks with different widths. In a semicrystalline polymer above its glass transition temperature, each crystallite is surrounded by the rubbery polymer in its equilibrium state and, so, each crystallite experiences the same potential field. If all the crystallites are of the same size, they would be associated with the same surface energy. These crystallites will then melt at the same temperature, giving a sharper peak with a larger amplitude. On the other hand, if there is a wide distribution of crystal sizes, the melting event will be spread over a broad temperature range, giving rise to a wider melting peak with a smaller amplitude. A high-resolution imaging study on the present samples will help to throw some light on these speculations and also help in establishing any parallels in the crystallization and double melting behaviors of PEEK and MePEEK.

CO_2 has no dipole moment and only a small quadrupolar moment and, therefore, is essentially a nonpolar fluid. The addition of a small amount of a polar cosolvent is equivalent to giving the mixed fluid an overall small dipole moment. The critical temperature and dipole moments of CH_2Cl_2 and CH_3OH are 237.0 °C and 1.8 D (Debyes) and 239.6 °C and 1.7 D, respectively. Adding 10 mol % of either of these liquids to CO_2 would then produce a supercritical fluid with the same overall critical temperature and dipole moment. At a fixed composition, the corresponding states theory, in fact, predicts very similar properties for the two binary fluids. The different crystallization behaviors observed with the two binary fluids cannot then be attributed to any differences in their critical properties or polar characteristics. The fluids, however, may differ in their solvation characteristics. There is another possibility. The binary fluids were obtained as compressed liquid mixtures in cylinders with compressed helium head space and siphon tubes. The mixture is drawn off the cylinder as a liquid and goes into the supercritical state after it enters the oven. With use, there will be enrichment of the less volatile component in the cylinder and this enrichment will be more for the mixture containing CH_3OH than for the one containing CH_2Cl_2. So, even if the original cylinders as purchased from the supplier contained 10 mol % of the cosolvent, it is very likely that after some use the cosolvent content will be higher than 10% and that this increase will be higher in the case of CO_2 + CH_3OH than in the case of CO_2 + CH_2Cl_2. Consequently, a slightly larger fraction of the polar component will be delivered to the polymer matrix in the case of CO_2 + CH_3OH than in the case of CO_2 + CH_2Cl_2, and the effect induced by the polar cosolvent will be more pronounced in the former case. A supercritical fluid is able to penetrate and distribute itself uniformly throughout the amorphous polymer matrix because of the high kinetic energy associated with it. The role of CO_2 is, in addition to its own plasticizing effect, to act as a carrier and deliver uniformly the polar component to the polymer matrix. It therefore appears that the presence of a polar cosolvent leads to a more homogeneous distribution of crystallites than what is obtained by CO_2 or thermal treatment alone. The enhanced stability observed in the case of CO_2 + CH_3OH may be because more CH_3OH molecules were delivered to the polymer matrix and/or the solvation characteristics of CH_3OH are quite different from those of CH_2Cl_2.

Smoothed X-ray diffraction patterns for the stepwise treated samples are presented in Figure 8 along with the sample as synthesised, labeled *untreated*. The treated samples show well-defined crystalline peaks overriding the amorphous background. The untreated sample gives the usual amorphous halo, and this pattern was used as a model to subtract out the amorphous contribution to the diffraction patterns for the semicrystalline samples. The residual patterns and the patterns in Figure 8 were then used to calculate the crystallinity values for the various samples. These results are summarized in Table 1 along with the densities, ρ. The ΔH and ρ values are expressed in terms of unit mass of the semicrystalline sample. Supercritical fluids are known to dilate the amorphous fraction of a semicrystalline polymer.[28] As a result, the density of the polymer crystallized using a supercritical fluid can be lower than when it is crystallized using thermal treatment alone.[21] In the present case, the densities of all the semicrystalline samples can be regarded to be within experimental precision. It should be noted that there is an error of about 5% associated with the calculation of the crystallinity values from the present X-ray diffraction data. This error arises from the noise in the diffraction data and from calculation of the amorphous contribution to the composite diffraction pattern. Consequently, we consider the crystallinity values in all the treated samples to be approximately the same. This is supported by the constancy of the ΔH values and, to a large extent, by the constancy of the density values. The results in Table 1 can be averaged to give 1.264 g cm^{-1} and 20.0 J g^{-1} for the density and heat of melting, respectively, for a sample of 27% crystallinity. In averaging the ΔH values, we have assumed that the change in heat capacity associated with the crystal $\rightarrow$ liquid transition is negligible. These results then give 1.348 g cm^{-3} and 74.0 J g^{-1} for the density and heat of melting of 100% crystalline MePEEK. The corresponding values[1] for PEEK are 1.40 g cm^{-3} and 130 J g^{-1}.

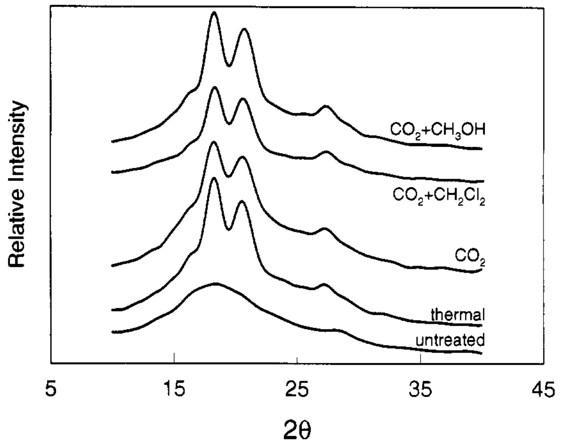

Figure 8. Smoothed X-ray diffraction patterns for the amorphous MePEEK, labeled *untreated*, and for the semicrystalline samples obtained by the stepwise treatments reported in Figure 7.

The main focus of the present investigation was to establish that supercritical fluids can be used for inducing crystallinity in a controlled manner in MePEEK. X-ray diffraction measurements were not performed on all the semicrystalline samples prepared in this work. A systematic investigation on samples covering a wider crystalline range would be highly desirable in estbalishing more accurately the ρ and ΔH values for the 100% crystalline MePEEK.

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