

PEEK Oligomers: A Model for the Polymer Physical Behavior. 3. Nature of Oligomers in the PEEK Polymer

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ABSTRACT: Low molecular weight compounds extracted from PEEK have been identified by ^{13}C NMR, infrared spectroscopy, and size-exclusion chromatography as being cyclic PEEK oligomers. The molecular weight of these cyclic oligomers is larger than 1000. Their wide-angle X-ray scattering powder pattern and crystal habit are totally different from those of the polymer. DSC experiments reveal that the oligomers crystallize in two different crystal types. The nucleation rate of these crystals is rather slow because of the large size of the molecules which have to be incorporated in the nucleus. Consequently, moderate cooling rates give rise to glassy oligomers. A very high T_g value is observed for the oligomers, in accordance with their low configurational entropy in the amorphous state due to their cyclic structure.

Introduction

Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (commonly known as PEEK) is an aromatic thermoplastic whose morphology has been much debated in recent years. This is due in part not only to the technological importance of this material but also to the fact that PEEK exhibits some properties which challenge our present knowledge of semicrystalline morphology. For instance, the PEEK double-melting behavior in relation to the possible existence of multiple lamellar populations has attracted much attention these last few years.¹

Recently, we conducted research on PEEK linear monodisperse oligomers,^{2,3} as part of a program devoted to a better understanding of PEEK physical properties. The complex melting behavior of these structurally simple compounds was tentatively related to differences in the relative placement of ether and ketone bridges in the crystal. Although basically different from the polymer double-melting behavior, the complex melting of the oligomers reflects the parallel complexity of the PEEK crystal structure, in accordance with theoretical predictions.⁴

In the present paper, we make use of some of the information gathered previously on PEEK oligomers to elucidate the exact nature of the low molecular weight compounds observed in the polymer molecular weight distribution.⁵ Specifically, we examine whether these low molecular weight compounds could act as polymer nucleating agents, as suggested by us previously.⁵ Some complementary results concerning the structure and thermal properties of these compounds are also briefly presented.

Experimental Section

PEEK (commercial grade 150P) was kindly furnished by ICI. Previously determined molecular weights are $M_n = 10\,300$, $M_w = 26\,800$, and $M_z = 52\,200$. The polymer was refluxed for 1 week with distilled acetone in a Soxhlet. The solution was hot-filtered, and subsequent recrystallization of the extracted low molecular weight compounds was observed at room temperature. Around 100 mg of small crystals could be collected from 50 g of polymer refluxed in 1 L of acetone. The extraction is also possible with methanol, but the process is slower.

^{13}C NMR was performed in methanesulfonic acid on a Bruker AM500, operated in the broad-band mode. The pulse width was 8 μs , the relaxation delay 3 s, the scan frequency 125.76 MHz, and the concentration 20 mg mL⁻¹.

Size-exclusion chromatography (SEC) of the extracted compounds was performed at 115 °C in a 50/50 w/w phenol/trichlorobenzene eluant as described elsewhere.⁶ The observed peak retention times were used to compute a molecular weight expressed in linear PEEK oligomer (LPO) equivalents, with reference to a calibration curve between retention time and molecular weight obtained from our previous study.² Room-temperature SEC of the sulfonated polymer before and after extraction was performed in *N*-methyl-2-pyrrolidone, as described elsewhere.⁷

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC2 at various heating rates. The base line was corrected for slope and balance, and the temperature calibrated with indium and zinc standards. Temperatures corresponding to the onset of phase transformation and to the peak value were recorded for each endotherm or exotherm.

Wide-angle X-ray scattering (WAXS) powder patterns were obtained at 21 °C with a Siemens D500 diffractometer, equipped with a graphite secondary monochromator. The powder diffractograms were obtained between 6 and 60° (2 θ), using Cu K α radiation (1.5418 Å), with a scan rate of 0.5° (2 θ)/min.

Results and Discussion

Spectroscopic Characterization. The ^{13}C NMR spectrum (top curve) of the extracted compounds is compared in Figure 1 with the spectra of a monodisperse fluoroaryl ketone-ended linear oligomer² (MW 1371, middle curve) and of the parent polymer (bottom curve). The extracted compounds have the same main resonances as the linear oligomer or the parent polymer. However, there is no evidence of any chain-end ^{13}C resonance for the extracted compounds, although both the parent polymer and the linear oligomer clearly exhibit such chain-end resonance. Infrared analysis confirms these observations: the absorption bands of the extracted compounds are the same as those of the PEEK repeating unit, but none of the chain-end bands found for the linear oligomers² can be detected in the spectrum of the extracted compounds.

The molecular weight number distribution of the parent polymer before and after extraction is presented in Figure 2. As expected, the extraction process reduces the amount of low molecular weight species in the polymer. By subtracting the two distributions after normalization to

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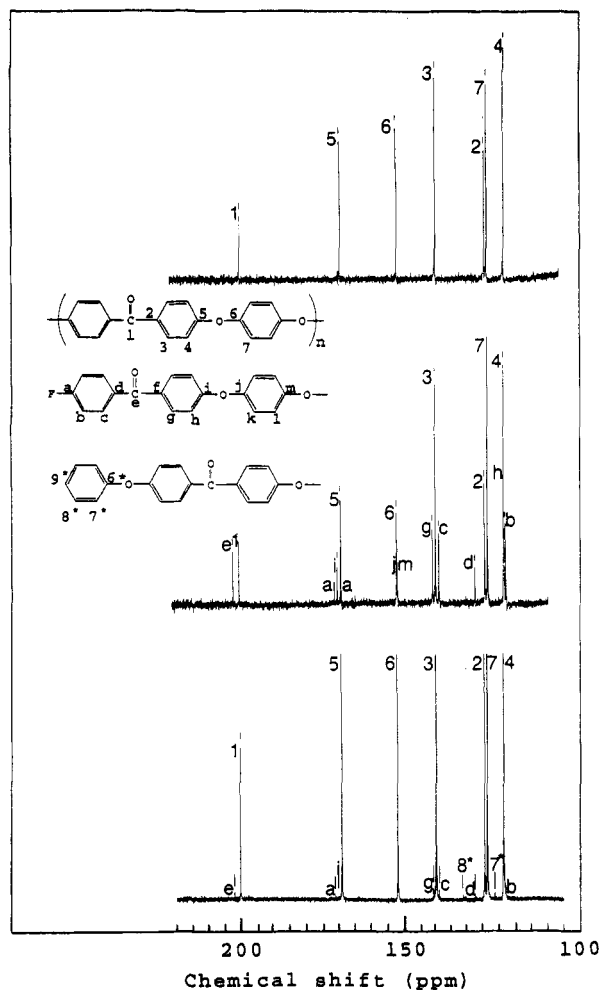


Figure 1. ^{13}C NMR spectra of the extracted oligomers (top), of a linear monodisperse oligomer synthesized in our laboratory² (middle), and of the parent PEEK (bottom). Contrary to the $\sim 10\,000$ molecular weight polymer and to the 1371 molecular weight linear oligomer, the extracted oligomers do not show any chain end peaks.

equal main peak height, the molecular weight number distribution of the extracted compounds could be estimated (inset, Figure 2). The peak value of the resulting narrow distribution corresponds to MW ~ 1090 . A narrow peak is also obtained when one performs high-temperature SEC directly on the extracted compounds. In this case, the molecular weight computed from the peak retention time is situated between 930 and 1030 (LPO equivalents). Upon careful inspection, a small shoulder can be detected on the main retention peak, suggesting that the extracted oligomers might not be monodisperse.

From the previous body of evidence, one can safely conclude that the extracted compounds are PEEK cyclic oligomers. Because of their cyclic nature, their retention times are expected to be higher than the retention times of linear oligomers of the same molecular weight. Hence, their actual molecular weight must be higher than the 1000 we derived from calibrations performed with linear oligomers or polymers. These oligomers thus contain at least four repeating units. Note that attempts to evaluate the absolute molecular weight of these cyclic oligomers using mass spectroscopy have not been successful so far.

The formation of cyclic oligomers during polycondensation is well-documented.⁸ Most polycondensate polymers contain such cyclic oligomers. This is the case for example for various polyesters like poly(ethylene terephthalate).⁹ The cyclic oligomer formation is controlled by the probability that two chain ends belonging to the

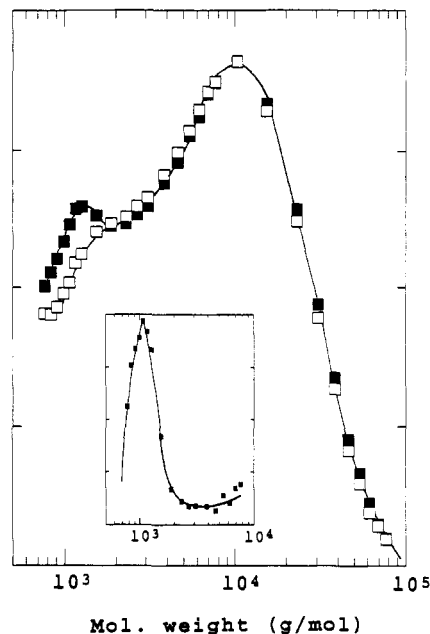


Figure 2. Number distribution of the PEEK molecular weight, obtained by room-temperature SEC: \blacksquare , original PEEK; \square , the same polymer after acetone extraction. Acetone extraction reduces the oligomer peak. Inset: difference between the two distributions.

same molecule react together during the polycondensation. This probability is highest for short chains above a threshold length. If during chain growth no mechanism is able to reopen previously formed cyclics, a significant amount of cyclics will be present in the final polymer. For cyclic aromatic polyethers produced by nucleophilic substitution, ether exchange reactions are the most probable ring-opening mechanism; however, these reactions are of minor importance in the case of PEEK,⁷ which probably explains the relatively large amount of cyclics found in this polymer.

Structural Characterization. The WAXS powder pattern of the acetone-recrystallized cyclic oligomers is presented in Figure 3 (top curve). The powder diffractogram of a linear monodisperse oligomer³ of MW 1371 is also reported for comparison purposes (bottom curve). The linear oligomer pattern is almost identical to the polymer patterns published in the literature.¹⁰ By contrast, the pattern of the cyclic oligomers is strongly distinct from that of the linear oligomer. It was not possible to compute the type and dimensions of the unit cell of the cyclic oligomers, probably because the acetone-crystallized powder is a mixture of different crystal types (see below). However, it is evident that none of these cyclic oligomers is large enough to pack into the linear PEEK crystalline cell.

In accordance with the WAXS results, we found that the crystal habit of the cyclic oligomers is different from that of the linear oligomers. A scanning electron micrograph (SEM) of a particularly well-developed cyclic oligomer crystal is presented in Figure 4. The angle between the boundary planes is $62\text{--}63^\circ$, while the angles between prominent faces of linear oligomer crystals are 0° , 90° , and $\sim 37.5^\circ$. Hence, the WAXS and SEM results both indicate that the PEEK cyclic and linear oligomers crystallize in widely distinct packings. Therefore, we can safely reject our previous suggestion that the cyclic oligomers could act as nucleating agents for the linear polymer.

Thermal Behavior. Figure 5 displays typical thermograms of the acetone-crystallized cyclic oligomers for

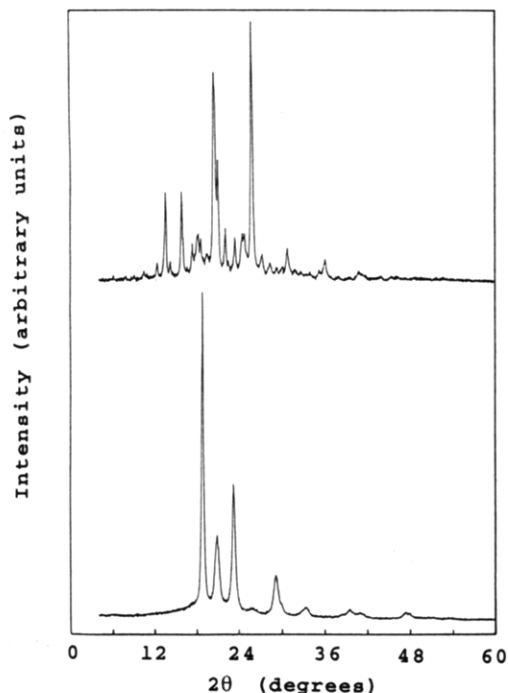


Figure 3. Powder diffractograms of the extracted oligomers (top curve) and of a 1371 molecular weight linear PEEK oligomer (bottom curve). The two crystalline packings are totally different, in accordance with the cyclic nature of the extracted oligomers.

various heating rates. As there is some evidence that the extracted cyclic oligomers might not be monodisperse, caution should be exercised when interpreting these curves. Anyway, it is clear that the oligomer mixture crystallizes into at least two crystal types, the first one melting in the range 315–320 °C and the second one around 332 °C. A rapid recrystallization of type I crystals into type II crystals occurs immediately after their melting. For slow heating rates, the melting of type I crystals occurs almost simultaneously with the recrystallization of the produced molten phase into type II crystals, leading to a zero net energy balance with no melting endotherm or crystallization exotherm detected. As the heating rate increases, the recrystallization process takes place at increasingly higher temperatures, since temperature evolves now more rapidly during the induction time between melting and recrystallization, and type I crystal melting is more easily

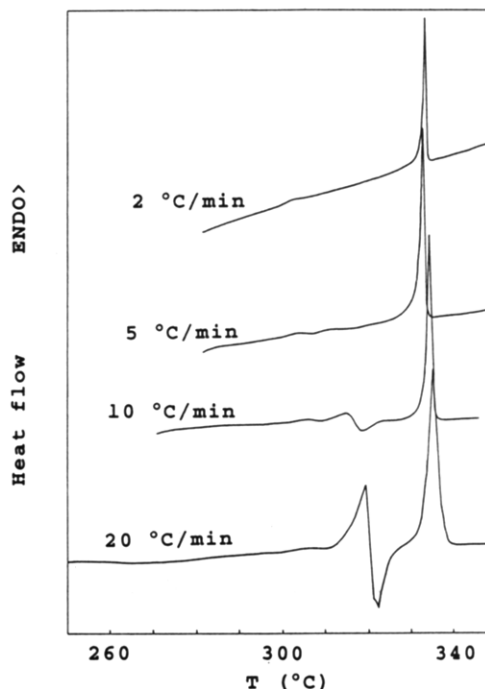


Figure 5. DSC thermograms of the cyclic oligomers (recrystallized from acetone). The heating rates are (from top to bottom) 2, 5, 10, and 20 °C min⁻¹. The melting of two crystal types is detected by DSC.

detected. If the oligomers are heated after having been crystallized by cooling from the molten state, only the melting of type I crystals can be detected (Figure 6.3). Actually, we found that only type I crystals are produced from the molten state, whatever the selected crystallization conditions. We clearly do not have enough experimental results to attribute the double-melting behavior of the cyclic oligomers to precise morphologies. We speculate that the origin of this behavior is similar to what has been found for linear oligomers,³ namely, different relative placements of the ether and ketone bridges in the crystals.

The mean value of the cyclics melting enthalpy (ΔH_m) is $74.6 \pm 2.9 \text{ J g}^{-1}$. This is roughly half the value reported for the melting enthalpy of fully crystalline PEEK (130 and 161 J g⁻¹).^{11,12} Since the melting temperature T_m of the extracted oligomers is almost as high as the polymer T_m , their melting entropy must be approximately half the

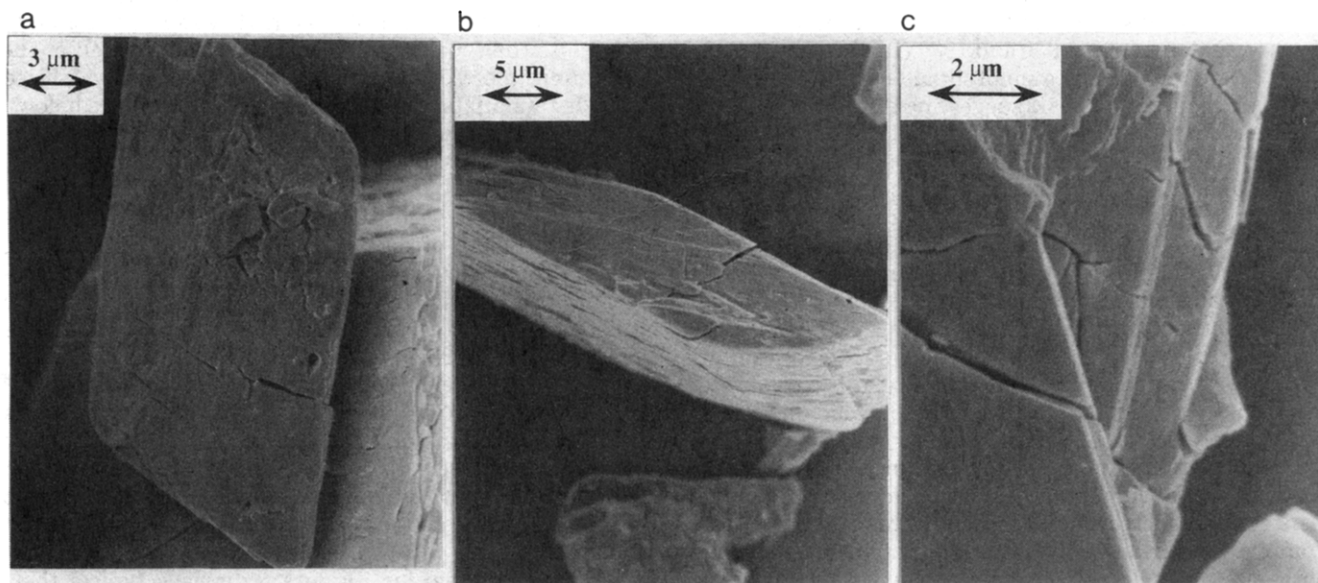


Figure 4. SEM microphotographs of a particularly well-developed oligomer crystal at various magnifications.

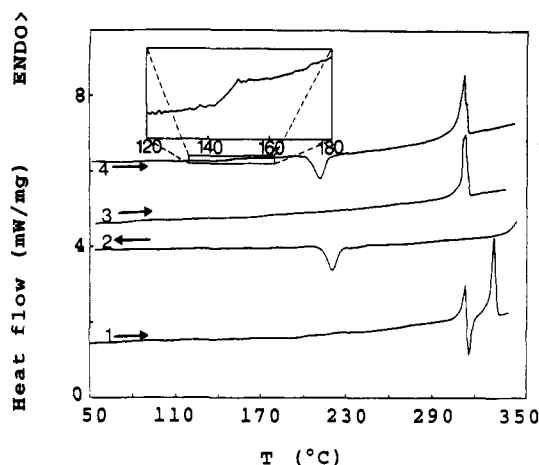


Figure 6. Thermal behavior of the cyclic oligomers ($10^{\circ}\text{C min}^{-1}$). Curve 1: heating scan of the original acetone-recrystallized oligomers. Curve 2: crystallization on cooling after a 45-s holding time in the melt at 342°C . Curve 3: subsequent heating of these melt-crystallized oligomers. Only type I crystals are detected. Curve 4: heating thermogram of the oligomers rapidly cooled from the melt. A glass transition is observed, followed by crystallization and melting of type I crystals. Inset: expanded view of the glass transition region of curve 4.

polymer melting entropy, in agreement with their cyclic nature.

When the oligomers are cooled at $10^{\circ}\text{C min}^{-1}$ from the molten state (342°C , 45 s), a 38.6 J g^{-1} crystallization exotherm is observed at 226.5°C (onset) (Figure 6.2). This is a very low crystallization temperature (T_c) by comparison with $T_c = 310^{\circ}\text{C}$ observed for the polymer crystallized in the same dynamic conditions or even $T_c = 270\text{--}290^{\circ}\text{C}$ measured for linear oligomers of $\sim 1000\text{--}1400$ molecular weight, which have lower T_m . Since the melt viscosity of the cyclic oligomers is certainly not larger than the viscosity of an entangled polymer melt, this dramatic decrease of crystallization kinetics must be associated to nucleation phenomena. Obviously, by the very nature of the extraction process, the extracted oligomers contain less heterogeneous nucleating seeds than the parent polymer. But this holds also true for the linear oligomers which were recrystallized in distilled solvents. Hence, the sluggish crystallization of cyclic PEEK oligomers is probably mainly due to the larger size of the elements required to build the crystalline lattice of the cyclics: the critical nucleus size is scaled accordingly. Although the polymer chains are much larger than the cyclic oligomers, it is easier to build a small nucleus having the proper crystalline packing by picking at random short linear segments from different long chains than by stacking correctly large cyclic molecules. Consequently, the probability to have a proper fluctuation in the melt will be significant only at much lower temperatures for the cyclic oligomers. This interpretation is further supported by the presence of numerous reflections at low angles in the WAXS pattern of the cyclic oligomers, which indeed suggests that some of the unit cell dimensions of these compounds are quite large.

Because of this slow nucleation rate of cyclic oligomer crystals, it is possible to obtain a fully amorphous glassy sample by cooling the oligomer melt rapidly in the DSC. A subsequent $10^{\circ}\text{C min}^{-1}$ thermogram is shown in Figure 6.4. The glass transition temperature (T_g) of the extracted oligomers is located at 144.5°C (midpoint), slightly higher than the T_g of the fully amorphous parent polymer (143.1°C). This can be explained with the aid of the Gibbs-Di Marzio thermodynamic theory of the glass transition:¹³ because the configurational entropy of cyclic oligomers in

the amorphous state is smaller than the configurational entropy of linear ones at the same temperature, the T_g of cyclic oligomers is higher than the T_g 's of linear oligomers of the same molecular weight and even possibly than the polymer T_g . A similar observation has been reported recently for cyclic polystyrene oligomers.¹⁴

Conclusions

By combining ^{13}C NMR, infrared analysis, and SEC, we have shown that a significant amount of cyclic oligomers can be extracted from PEEK ($\sim 0.2\text{ wt } \%$). Other observations confirm the cyclic nature of the extracted compounds, namely, their high T_m associated with a low melting enthalpy, their sluggish nucleation rate, and their high T_g .

These oligomers crystallize at least in two crystal types. The first type is obtained from solution crystallization and from crystallization from the amorphous state, while the second one can only be obtained from solution crystallization. The origin of these two crystal types was not elucidated in this paper, but we tentatively suggest that they could result from different relative placements of ether and ketone bridges in the crystal, similar to what we reported for the linear oligomers.³

The slow nucleation rate of the extracted cyclic oligomers implies they do not play any role in the crystallization kinetics of the polymer. Moreover, their crystalline packing is totally different from the polymer crystalline packing. This is a second reason for rejecting them as potential nucleating species for the polymer. Moreover, the easy way by which these oligomers can be extracted suggests that they are probably not crystalline in the original polymer powder.

Further research should nevertheless be carried out in the field of cyclic PEEK oligomers. If larger cyclic oligomers could be isolated, invaluable information could hopefully be obtained on the possible fold conformations of PEEK linear chains at the crystallite surfaces. It might also be interesting to evaluate the possibility of generating the polymer by ring-opening polymerization of such oligomers, a process which could be of significant importance because of the tough technological problems encountered when processing linear PEEK.

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