Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 1543–1552

polymer

www.elsevier.com/locate/polymer

Unusual thermal relaxation of viscosity-and-shear-induced strain in poly(ether-ketones) synthesized in highly viscous polyphosphoric acid/P_2O_5 medium

Jong-Beom Baek[a,c,*], Soo-Young Park[b], Gary E. Price[c], Christopher B. Lyons[d], Loon-Seng Tan[e,*]

[a] *School of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk 361-763, South Korea*
[b] *Department of Polymer Science, Kyungbuk National University, Taegu 702-701, South Korea*
[c] *University of Dayton Research Institute, 300 College Park, Dayton, OH 45469-0168, USA*
[d] *Southwestern Ohio Council for Higher Education, 3155 Research Boulevard, Suite 204, Dayton, OH 45420-4015, USA*
[e] *Polymer Branch, Materials and Manufacturing Directorate, AFRL/MLBP, Air Force Research Laboratory, Wright-Patterson Air Force Base, Dayton, OH 45433-7750, USA*

Received 21 July 2004; received in revised form 7 December 2004; accepted 15 December 2004
Available online 13 January 2005

Abstract

We recently described an improved method to synthesize poly(ether-ketones) or PEKs. It utilized an optimized mixture of polyphosphoric acid (PPA) and P_2O_5 that is not only milder, less corrosive and less expensive than super-acid media, but also can play the multiple roles of solvent, Friedel–Crafts catalyst and dehydrating agent. The as-prepared PEKs from such a highly viscous reaction medium displayed unexpected, thermally induced relaxation exotherms regardless of the amorphous or semi-crystalline nature of polymer. This thermal behavior was not observed for the formally identical polymers [viz. *p*PEK or poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene] which is normally semi-crystalline) that were separately prepared in a much less viscous mixture of methanesulfonic acid and P_2O_5 (Eaton's reagent) or *N*-methyl-2-pyrrolidinone (NMP). Such an observation was first made when both samples of *p*PEKs were subjected to the same thermal history and the thermal relaxation exotherms were observed only for the *p*PEK sample that was prepared in PPA/P_2O_5 medium. Further confirmation of viscosity-and-shear-induced strain stored in the as-synthesized PEKs was provided by a systematic annealing study with differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) analysis and Fourier-transform infrared spectroscopy (FT-IR). Based on these data, *p*PEK was successfully compression-molded in the temperature range of 230–250 °C which is more than 100 °C below its melting temperature.

Keywords: Friedel–Crafts acylation; Thermal analysis; Wide-angle X-ray diffraction

1. Introduction

Poly(ether-ketones), or PEKs, are an important family of engineering thermoplastics with a good balance of material properties and processing characteristics [1]. There are two general synthetic pathways to producing PEKs, namely, aromatic electrophilic substitution (Friedel–Crafts acylation) and aromatic nucleophilic substitution reactions. The aromatic electrophilic substitution polycondensation involves an aromatic bis(carboxylic acid) or bis(acid chloride) and bis(phenoxy) monomers [2] as well as a need for strongly corrosive acid systems such as boron trifluoride/hydrofluoric acid [3,4] phosphorous pentoxide(P_2O_5)/methanesulfonic acid (MSA) [5], aluminum chloride/polyphosphoric acid (PPA) [6] and trifluoromethanesulfonic acid [7]. The base-promoted aromatic nucleophilic substitution polymerization require the salt form of bis(phenol) and activated halogen- or nitro-containing

---

* Corresponding authors. Tel.: +1 937 255 9141; fax: +1 937 255 9157.
E-mail addresses: jbbaek@chungbuk.ac.kr (J.-B. Baek), loon-seng.tan@wpafb.af.mil (L.-S. Tan).

0032-3861/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.polymer.2004.12.022

monomers [8,9]. While each method has its own merits and drawbacks, aromatic nucleophilic substitution reactions are generally the more preferred route because of the availability of suitable monomers, non-corrosive reaction media, and the operational convenience in conducting the synthesis.

Recently, we have reported an improved electrophilic substitution route utilizing polyphosphoric acid/phosphorus pentoxide, PPA/P_2O_5, as a polymerization medium that is relatively less corrosive, non-toxic, and non-volatile to prepare high molecular-weight PEKs from several AB monomers containing arylether (A) and carboxylic acid (B) groups [10]. Similar to the super-acid systems, this versatile polymerization medium acts in the multiple roles of solvent, acylation catalyst and dehydration agent, and was also successfully applied to the syntheses of various macromolecular systems such as ABA block copolymers [11] and hyperbranched polymer [12] as well as the functionalization [13] and grafting [14] of vapor-grown carbon nanofibers. During the course of our synthesis efforts, we have unexpectedly uncovered the fact that the polymerization medium, PPA/P_2O_5, is highly viscous and thus could result in a vastly different morphology in the synthesized PEK as compare to that prepared in less viscous media such as Eaton's reagent (8–10 wt % P_2O_5 in methanesulfonic acid) for aromatic electrophilic substitution process or in polar aprotic solvents for nucleophilic substitution process [15].

In this paper, we report our observation of an unusual, thermal relaxation phenomenon that has occurred in the as-synthesized PEKs during the post-polymerization heat-treatment. Specifically, our polymerization conditions are such that the inherently semi-crystalline *p*PEK was amorphous and maintained its amorphousness even after polymerization and work-up processes, and only reverted to its semi-crystalline state after heat-treatment. Thus, an important implication is that the semi-crystalline *p*PEK could be compression-molded in the range of temperatures above its T_g but well below its melting temperature, which is near its degradation temperature.

2. Experimental

2.1. Materials

All reagents and solvents were purchased from Aldrich Chemical Co. and used as received, unless otherwise specified. Methanesulfonic acid (MSA) was distilled under reduced pressure prior to use. The AB-monomers, 3-phenoxybenzoic acid and 4-phenoxybenzoic acid, were purified by recrystallization from toluene/heptane (1/1, v/v) mixture to give shiny colorless needles (m.p. 147–148.5 °C and 162–164 °C, respectively) with 99.99+% purities (HPLC). Phosphorus pentoxide in MSA solution or PPMA (available commercially as Eaton's Reagent, 7.7 wt % of P_2O_5 in MSA) was used as received.

All PEKs via electrophilic substitution reactions were prepared as described previously in the literature in the most viscous medium, PPA/P_2O_5 (4/1, w/w) [1] or moderately viscous Eaton's reagent (MSA/P_2O_5) [16]. *p*PEK derived from 4-fluoro-4′-hydroxybenzophenone via nucleophilic substitution reaction was prepared in the least viscous NMP/toluene mixture in the presence of potassium carbonate [17].

The same work-up procedure was followed for all polymerizations to ensure identical handling and thermal history for all polymer samples. Thus, after each polymerization reaction, the precipitated polymer product was Soxhlet-extracted with water for 100 h, followed by an additional extraction with methanol for 24 h, to remove all the residual salts, solvents and acids, from the samples which were finally dried under reduced pressure (1 mmHg) at 120 °C for 72 h before being used for characterization.

2.2. Polymerization in PPA/P_2O_5 (most viscous medium)

Into a 250 mL resin flask equipped with a high torque mechanical stirrer, and nitrogen inlet and outlet, PPA (83% assay, 80 g) was placed and stirred under dry nitrogen at 100 °C for 10 h. After each monomer [3-phenoxybenzoic acid (4.0 g, 18.7 mmol), 4-phenoxybenzoic acid (4.0 g, 18.7 mmol), 4-(2,6-dimethylphenoxy)benzoic acid (4.0 g, 16.5 mmol)] was added, the resulting mixture was heated again to 100 °C and kept at that temperature for about 1 h. P_2O_5 (20.0 g) was then added in one portion, and the temperature of the mixture was raised to and maintained at 130 °C for 6–12 h. The mixture became very viscous after a few hours at 130 °C and started to stick to the stirring rod. At the end of the polymerization, water was added to the flask. The resulting polymeric product was transferred to a Waring blender to be chopped, then collected by suction filtration. It was washed first with diluted ammonium hydroxide, then with large amount of water, which was followed by Soxhlet extraction with water for 100 h and with methanol for 24 h. It was finally dried in the presence of phosphorous pentoxide under reduced pressure (1 mmHg) at 120 °C for 72 h. The yield of *m*PEK **1a** (fibrous, purple solid) was essentially quantitative (>99% yield) with determined intrinsic viscosity of 2.10 dL/g (MSA, 30±0.1 °C). Anal. Calcd for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 79.57%; H, 4.33%; O, 15.40%. Me_2-*p*PEK **2** was isolated as a fibrous, light pink solid in 84% yield. Its determined intrinsic viscosity was 0.76 dL/g (MSA, 30±0.1 °C). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34%; H, 5.39%; O, 14.27%. Found: C, 78.59%; H, 5.44%; O, 13.75%. The yield of *p*PEK (pink solid) **3a** was 75%. The intrinsic viscosity value of 0.69 dL/g (MSA, 30±0.1 °C) was determined. Anal. Calcd for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 78.91%; H, 4.25%; O, 15.88%.

2.3. Polymerization in PPMA (Eaton's reagent, moderately viscous medium)

Polymerization was carried out similar to the conditions described in the literature [18]. Into a 100 mL round-bottom flask with a magnetic stirrer, nitrogen inlet and outlet, PPMA (20 mL) and 3-phenoxybenzoic acid were placed and stirred under dry nitrogen atmosphere at 100 °C for 24 h. The resulting dark brown mixture was poured into ice water. The purple precipitates were collected by suction filtration and washed first with diluted ammonium hydroxide, then with large amounts of water, which was followed by Soxhlet extraction with water for 100 h, and then with methanol for 24 h. It was finally dried in the presence of phosphorous pentoxide under reduced pressure (1 mmHg) at 120 °C for 72 h to give 1.63 g (89% yield) of purple powder. The intrinsic viscosity value of 0.64 dL/g (MSA, 30 ± 0.1 °C) was determined. Anal. Calcd for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 76.71%; H, 4.26%; O, 15.33%.

2.4. Polymerization in K_2CO_3/NMP (least viscous medium)

Into a 100 mL three-necked, round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet and outlet, and a Dean-Stark trap with a condenser, 4-fluoro-4′-hydroxybenzophenone (3.0 g, 13.88 mmol), potassium carbonate (3.0 g, 21.7 mmol), and a mixture of NMP (30 mL) and toluene (60 mL) were introduced. The reaction mixture was then heated and maintained at 140–150 °C for 4 h. During this time, the water formed was removed by azeotropic distillation with toluene. After the complete removal of toluene by forceful nitrogen purging, the orange solution was then heated at 180 °C for 1 h. Finally, the mixture was heated to 202 °C. After 30 min, the mixture became heterogeneous. The mixture was stirred for additional 6 h, allowed to cool to room temperature, and poured into distilled water containing 5% hydrochloric acid. The resulting white precipitates were collected by suction filtration, Soxhlet extracted with water for 100 h and methanol for 24 h, and finally dried in the presence of phosphorous pentoxide under reduced pressure (1 mmHg) at 120 °C for 72 h to give a pale white powder. The yield was essentially quantitative; $[\eta]=0.85$ dL/g (MSA, 30.0 ± 0.1 °C); $T_m=360.5$ °C (DSC). Anal. Calcd for $C_{13}H_8O_2$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 77.34%; H, 4.52%; O, 15.35%.

2.5. Instrumentation

Infrared (IR) spectra were run on a ThermoNicolet Nexus 470 Fourier transform spectrophotometer. Intrinsic viscosities were determined with a Cannon-Ubbelohde No. 150 viscometer. Flow times were recorded for methanesulfonic acid (MSA) solutions with polymer concentrations of 0.5–0.1 g/dL at 30.0 ± 0.1 °C. Differential scanning calorimetry (DSC) was performed in nitrogen with a heating rate of 10 °C/min using a Perkin–Elmer model 2000 thermal analyzer. Wide-angle X-ray diffraction (WAXS) powder patterns were recorded with a Rigaku RU-200 diffractometer using Ni-filtered Cu Kα radiation (40 kV, 100 mA, $\lambda=0.15418$ nm). Scanning-electron microscopic (SEM) studies were conducted with Hitachi S2500C.

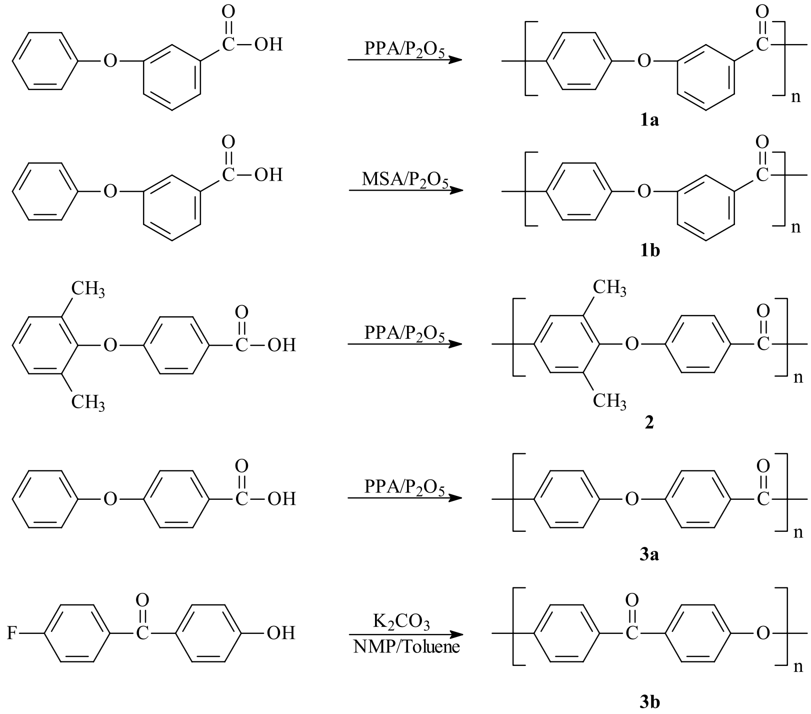
3. Results and discussion

3.1. Polymerization

Following the reported procedure [1], polymers *m*PEK (**1a**), Me_2-*p*PEK (**2**), and *p*PEK (**3a**) were prepared at 130 °C in PPA/P_2O_5 (in 4:1, w/w ratio; the most viscous medium) from the 3-phenoxybenzoic acid (3-PBA), 4-(2,6-dimethylphenoxy)benzoic acid (Me_2−4PBA), and 4-phenoxybenzoic acid (4-PBA), in that order, and in 5 wt % monomer concentration [19] that is relative to the amount of PPA used (see Scheme 1). For comparison purposes, polymers *m*PEK (**1b**), and *p*PEK (**3b**) were prepared from 3-PBA in Eaton's reagent (moderately viscous medium), and from 4-PBA in NMP/toluene solvent-mixture (the least viscous medium) (Scheme 1), respectively. The intrinsic viscosity and thermal properties of all the polymers are summarized in Table 1. In a synthesis experiment for the semi-crystalline *p*PEK **3a**, after the polymer/PPA dope had been precipitated into and soaked in a copious amount of water overnight, the resulting polymer was fibrous, practically transparent and colorless (see Fig. 1a). In contrast, the formally identical *p*PEK **3b** when isolated was a white and opaque powder. Subsequently, after a Soxhlet extraction with boiling water for 170 h, the *p*PEK **3a** sample still maintained its fiber form (Fig. 1b) but became somewhat less transparent [20]. During the aqueous work-up, a small amount of *p*PEK **3a** was isolated as small sheets from the wall of the polymerization vessel. From the surface of **3a** fiber, the small-pond-like microstructures (micro-voids) that were generated by dissolved PPA were observed (Fig. 1c, d). The presence of numerous micro-voids was not unexpected since 95% of the polymerization dope by weight was contributed by PPA/P_2O_5 mixture.

3.2. DSC Analysis

The DSC samples in powder form were subjected to at least two cycles of heating from room temperature to 320–400 °C and then cooling to 20 °C at the scanning rate of 10 °C/min for both heating and cooling cycles. For most samples, up to six cycles of combined heating and cooling runs were conducted in order to ascertain various types of observed thermal events. The T_g value was taken as the mid-point of the maximum baseline shift during each heating or cooling run. As shown in Fig. 2a and Table 1, the *m*PEK (**1a**) sample that was prepared in the most viscous medium,



Scheme 1. Synthesis of PEKs in reaction media with distinctly different viscosities.

PPA/P_2O_5 ([η] = 2.10 dL/g), exhibited a T_g at 137 °C. **1a** also displayed an unexpected, strong exotherm with peak value at 250 °C and with ΔH_{exo} = 18.7 J/g during the first run, and this exotherm was shifted to 305 °C during the second run. However, *m*PEK **1b** ([η] = 0.64 dL/g), prepared in a different reaction medium that was much less viscous (Eaton's reagent or MSA/P_2O_5), displayed no detectable exotherm. (Fig. 2b).

Me_2-*p*PEK **2**, namely the 2,6-dimethyl substituted version of *p*PEK **3**, was amorphous and displayed a similar relaxation exotherm maximizing at 216.0 °C (26.4 J/g) in the first heating run. The second heating run saw the disappearance of the exothermic peak and the presence of a T_g around 201 °C (Fig. 3).

The semi-crystalline *p*PEK **3a**, which was also prepared from the PPA/P_2O_5 route, displayed a broad melting endotherm centered at 344.3 °C (32.7 J/g) in the first heating scan (Fig. 4a, trace i). For the formally identical *p*PEK **3b**, a relatively sharp melting endotherm at 360.5 °C (36.9 J/g) was also observed in the first heating run (Fig. 4b, trace i). However, the value was 16 °C higher than that of **3a**. This is expected since **3b** was prepared from an aromatic nucleophilic substitution reaction [6], the stereo-specific nature of the reaction would dictate all para-substitution pattern that should result in a higher degree of crystallinity in **3b**. However, it was rather surprising to observe (Fig. 4a, trace i) that **3a**, apart from showing a T_g at 159.3 °C, displayed two exothermic peaks at 191.7 °C (20.7 J/g) and 275.3 °C (44.7 J/g) in the first heating run. An obvious explanation for the existence of these exotherms is that **3a** must have retained its amorphousness during the polymerization and work-up stages, and undergone a recrystallization process as indicated by the latter exotherm. This rationale is supported by the fact that **3b** showed a crystallization peak around 272 °C (Fig. 4b, trace ii). The origin of the first exothermic peak at 191.7 °C is likely

Table 1
Intrinsic viscosity and thermal properties of PEKs

Entry	[η]^a (dL/g)	T_g^{b} (°C)	T_{hc}^{b} (°C)	ΔH_{hc} (J/g)	T_m^{b} (°C)	ΔH_f (J/g)	T_{cc}^{c} (°C)	ΔH_{cc} (J/g)
1a	2.10	137	250	18.7	ND	ND	ND	ND
1b	0.64	129	ND	ND	ND	ND	ND	ND
2	0.76	200	216	26.4	ND	ND	ND	ND
3a	0.69	159	275.3	44.7	344	32.7	221.3	13.1
3b	0.85	175	ND	ND	361	36.9	272.0	34.6

[a] Intrinsic viscosity measured in MSA at 30 ± 0.1 °C.

[b] Glass transition temperature (T_g), crystallization temperature (T_{hc}), and melting temperature (T_m) determined by DSC with heating rate of 10 °C/min. ND = not detected.

[c] Crystallization temperature (T_{cc}) determined by DSC with cooling rate of 10 °C/min.

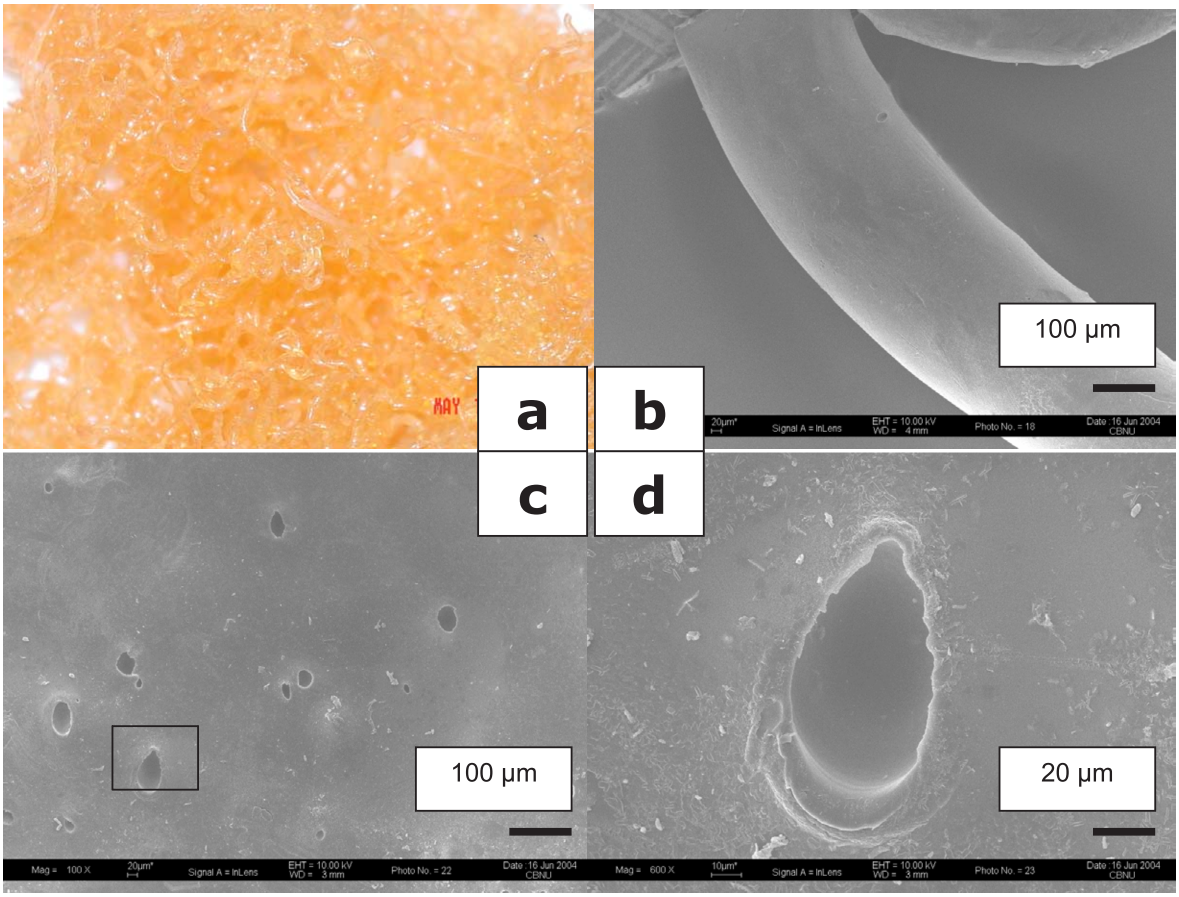


Fig. 1. (a) Digital photograph of an as-synthesized *p*PEK **3a** that had been precipitated and soaked in water overnight prior to Soxhlet extraction to remove the residual phosphoric acid. The isolated *p*PEK **3a** was fibrous, colorless and transparent as a result of its highly amorphous state; (b) SEM image (100×) of a single *p*PEK **3a** fiber from (a); (c) SEM image (100×) of a *p*PEK **3a** sheet after Soxhlet extraction; (d) magnified SEM image (500×) of (c).

related to the enthalpy released from a relaxation (strain-releasing) process similar to but not as symmetrical as the relaxation exotherms that were also observed for *m*PEK (**1a**) and Me$_2$-*p*PEK (**2**) in the same temperature neighborhood (see Figs. 2a and 3).

From the foregoing DSC results, we propose the following scenario: the isolated *p*PEK **3a** was strained because of shear field generated by the mechanical stirring in PPA/P$_2$O$_5$. It remained trapped in this strained state in the PPA/P$_2$O$_5$ continuous phase during the polymerization stage because of the viscosity-imposed molecular confinement, as illustrated in Scheme 2 [21]. After polymerization had been completed, water was added to the reaction mixture to readily dissolve PPA/P$_2$O$_5$ medium and precipitate the colorless and transparent polymer (see Fig. 1). Apparently, the kinetic barrier was high enough such that the as-synthesized *p*PEK **3a** must be largely still in the strained state even after initial and prolonged heat-treatment, i.e. continuous Soxhlet extraction with water and vacuum-drying, at temperature (100–120 °C) well below certain critical temperature (*vide infra*). Thus, in the pertinent DSC experiment, when the heating temperature approached 190 °C, the rate of relaxation presumably reached its maximum to allow *p*PEK **3a** to arrive at the unstrained state with the concomitant release of strain enthalpy. This is nicely shown by comparing the DSC results for both **3a** and **3b**. On the first cooling scan (Fig. 4a, trace ii), **3a** displayed a broad, recrystallization exothermic peak at 221.3 °C (13.1 J/g), and a T_g at 159.5 °C while **3b** displayed a sharp recrystallization peak at 271.8 °C (34.6 J/g) and a T_g at 169.3 °C (Fig. 4b, trace ii). On the second heating run, **3a** and **3b** (Fig. 4a and b, traces iii) showed (a) T_g at 165.0 and 174.6 °C; (b) recrystallization exothermic peak at 227.0 °C and not detected; and (c) melting endothermic peak at 326.0 and 344.3 °C, in that order. In both cases (**3a** and **3b**), the values of melting enthalpy were significantly reduced upon repeated DSC scans. We suspect that the time required for *p*PEK to completely recover its crystallinity after melting would be much longer than it was allowed in our DSC experiments.

In addition, the following remarks may be made on the discrepancy in the thermal properties with respect to electrophilic versus nucleophilic routes to *p*-PEK **3**: (a) The broader and lower the melting temperature is, so is the

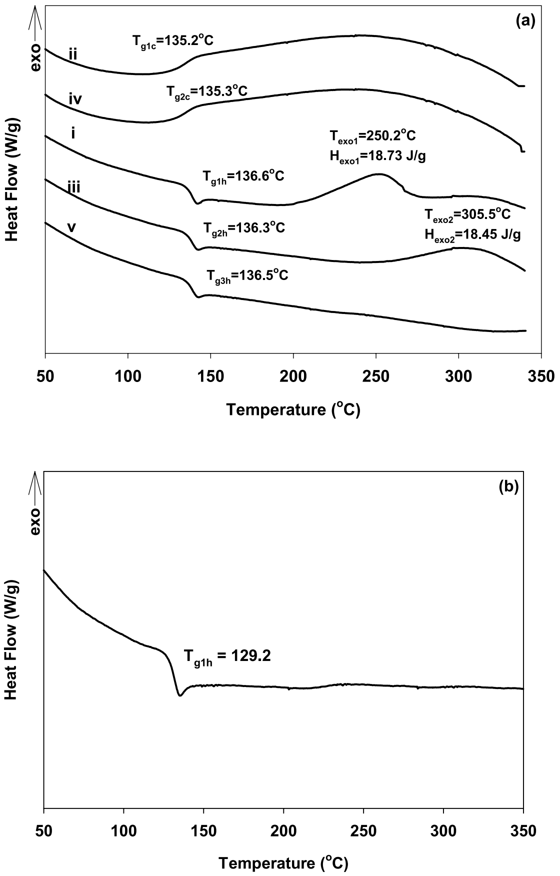


Fig. 2. DSC thermograms generated at heating and cooling rates of 10 °C/min: (a) *m*PEK, **1a**; (b) *m*PEK, 1b: (i) first heating; (ii) first cooling; (iii) second heating; (iv) second cooling; (v) third heating.

lower and broader the recrystallization temperature, and the slower the crystallization rate is; (b) we suspect that the lower T_g value in **3a** than that of **3b** ($\Delta = 19.3$ °C) may be originated from a small portion of ortho-substitution defects in the former [22].

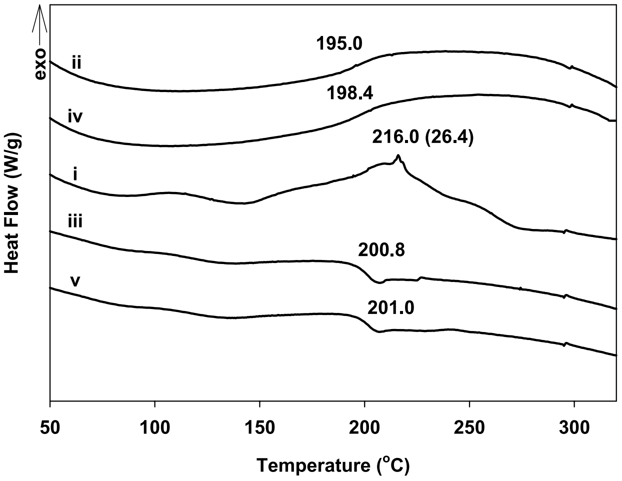


Fig. 3. DSC thermograms for Me$_2$-*p*PEK, 2 with heating and cooling rates of 10 °C/min: (i) first heating; (ii) first cooling; (iii) second heating; (iv) second cooling; (v) third heating.

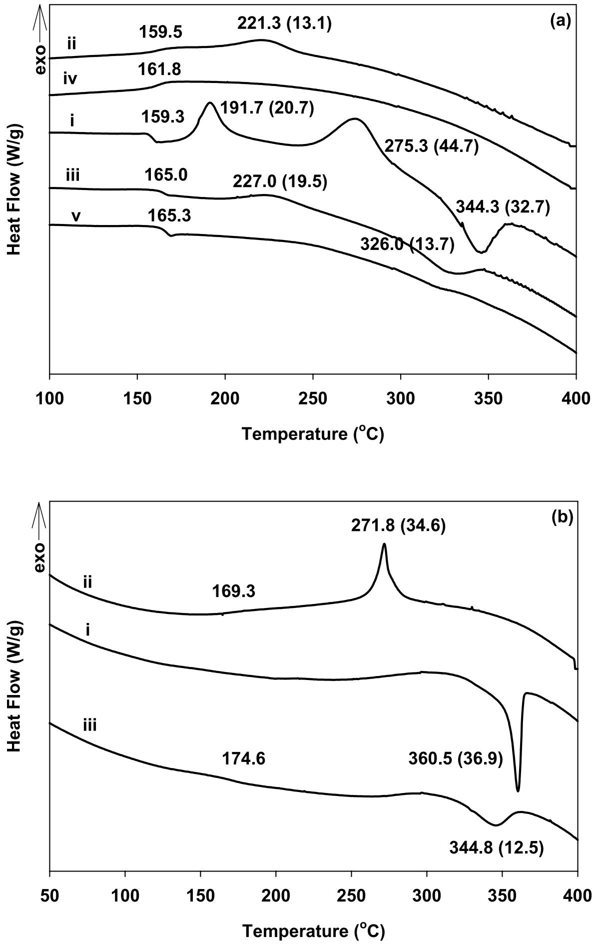
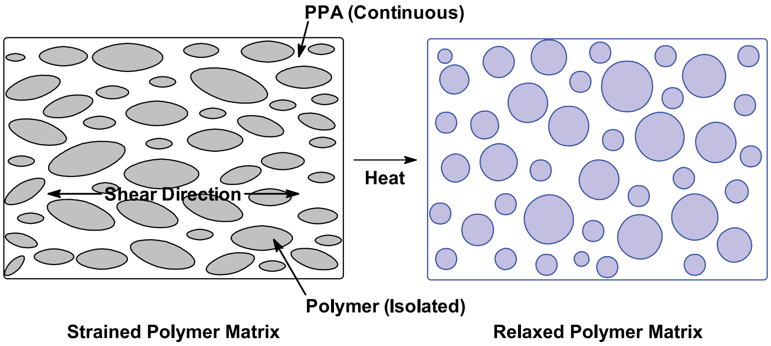


Fig. 4. DSC thermograms for polymers (a) **3a** and (b) **3b** with heating and cooling rates of 10/min: (i) first heating; (ii) first cooling; (iii) second heating; (iv) second cooling; (v) third heating. The T_g values in thermograms (b) were determined after zooming in the 150–200 °C region.

3.3. Annealing study of pPEK ***3a***

As an effort to shed further light on the thermodynamic driving force underlying the viscosity-suppressing crystallization of the semi-crystalline *p*PEK **3a**, we have conducted a systematic annealing study. Thus, three samples of **3a** were separately heat-treated at 190, 230, and 270 °C in vacuum (~1 Torr) for a 24-hour period for each temperature. The annealing temperatures were selected from where the exothermic peaks had appeared during the DSC heating scans from the pristine **3a**, (Fig. 4a).

The first sample that had been annealed at 190 °C displayed a T_g at 163 °C, two exothermic peaks at 191 and 276 °C, and a T_m at 340 °C during the first heating scan (Fig. 5a, trace i). The overall appearance of the DSC trace was quite similar to that of the un-annealed one (Fig. 4a, trace i). Thus, there was no major relaxation in **3a** induced by annealing at 190 °C. On the first cooling run (Fig. 5a, trace ii), the recrystallization occurred at 247 °C, which is about 25 °C higher than the untreated sample (Fig. 4a, trace ii), indicating that there existed some sort of local relaxation.



Scheme 2. Schematic presentation of thermal relaxation of viscosity- and shear-induced strain in PEKs synthesized in poly(phosphoric acid).

We believe that this would then play a nucleation role to trigger some short-range ordering that would eventually lead to a well-defined crystallization. On the second heating run (Fig. 5a, trace iii), both exothermic peaks had initially appeared on the first heating run vanished, the melting temperature shifted from 340 to 331 °C, and a T_g, was detected at 165 °C. On the third heating and cooling runs (Fig. 5a, traces v and vi) the crystal-melting and recrystallization temperatures shifted further down to 327 and 227 °C, respectively. The progressive depression of crystal-melting and crystal-forming temperatures could be influenced by the stability of crystals. We speculate that the time for the heat treatment at the scanning rate of 10 °C/min was not sufficient to allow for an uninterrupted crystallization process to take place, resulting in the observed melting-point depression.

For the second sample (annealed at 230 °C), its T_g could not be detected and the first exothermic peak disappeared while the second, though weaker, exothermic peak remained around 277 °C (Fig. 5b, trace i). It is noteworthy that the annealed material appeared to have lost its amorphousness, suggesting that a near-complete relaxation had happened at this annealing temperature. This sample also displayed a broad melting around 327 °C. On successive cooling runs (Fig. 5b, traces ii, iv and vi), the recrystallization temperature was depressed from 271 to 265 °C and then to 262 °C. The crystallization temperature in the first cooling scan is, however, about 50 and 25 °C higher than those of untreated sample and the sample annealed at 190 °C, respectively. The glass-transition and crystal-melting temperatures from the second and third heating runs remained almost identical (Fig. 5b, traces iii and v).

After the third sample had been annealed at 270 °C, its T_g also could not be detected. In addition, both the first and the second exothermic peaks associated with thermal relaxation and crystallization processes disappeared and a broad crystal-melting endotherm was found at lower temperature, ~319 °C (see Fig. 5c, trace i). On the cooling runs (Fig. 5c, traces ii, iv and vi), the depression trend of the recrystallization temperature with successive cycles was almost similar to that of the second sample annealed 230 °C (Fig. 5b, trace ii, iv and vi). The values for the melting temperature in the second and the third heating runs were also similar to those of the second sample.

In short, the first exotherm (max. 191 °C) in the first heating DSC scan (Fig. 5a, trace i) can be unequivocally attributed to the thermal relaxation associated with the strained *p*PEK chains that had been synthesized in the very viscous medium, PPA/P_2O_5 and under a constant shear field. This is significant in the sense that even though *p*PEK is inherently a semi-crystalline polymer, our polymerization conditions allow it to kinetically retain its amorphousness until the purposeful heat treatment. As an important consequence of this discovery, the amorphousness of as-synthesized *p*PEK would lend itself to melt processing options at lower-temperatures. Indeed, we have found that *p*PEK could be compression-molded around 230–250 °C. In view of the processing difficulties in *p*PEK because of its poor solubility and high melting temperature being too close to its thermal degradation temperature, our studies would provide a practical improvement, i.e. widening the processing window, in the solventless processing of *p*PEK.

3.4. Wide-angle X-ray diffraction (WAXD) study

Wide-angle X-ray powder diffraction patterns show that polymers **1a** and **2** to be amorphous with no distinct order present for their samples before and after annealing. The polymer samples **3a**, *p*PEK were subjected to heat treatment at 190, 230, and 270 °C for 24 h as described in DSC study, and then scanned with wide-angle X-ray to study the changes in its morphology as a function of annealing temperatures (Fig. 6). The as-synthesized **3a** showed its amorphous character in the WAXD, thus corroborating the DSC result (Fig. 5a). The sample that had been annealed at 190 °C indeed displayed a noticeable amount of ordering (32%), which would stem from the short-range ordering by local relaxation. When the sample was annealed at 230 °C, it had less order (11%) than that of as-synthesized **3a**, indicating that the local order attained by annealing at 190 °C is a meta-stable state, which could be partially destroyed at 230 °C. Finally, the sample was annealed at 270 °C, where the recrystallization of *p*PEK typically

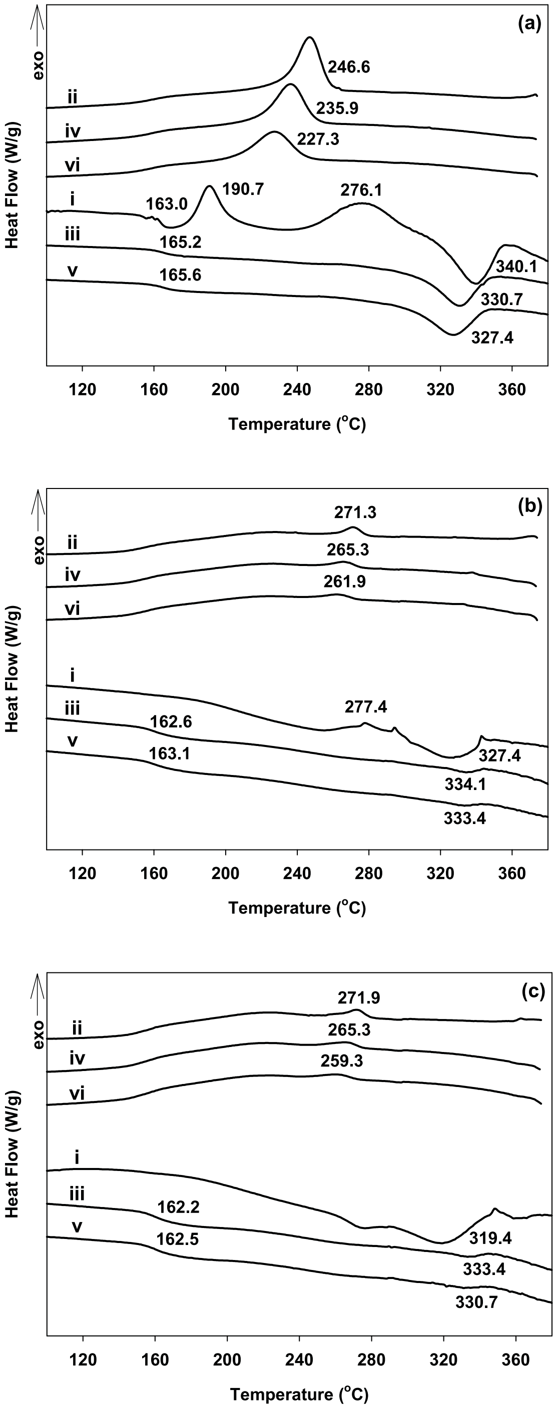


Fig. 5. DSC behaviors for **3a** after subjected to various annealing temperatures: (a) at 190 °C for 24 h; (b) at 230 °C for 24 h; (c) at 270 °C for 24 h: (i) first heating; (ii) first cooling; (iii) second heating; (iv) second cooling; (v) third heating; (vi) third cooling.

occurred (Fig. 4b). It displayed a larger degree of crystallinity (49%). *p*PEK **3a** displayed WAXD peaks at 2.69, 3.09, 3.83, 4.23, 4.67 Å (Fig. 7d), which are almost identical to the peak position observed for the **3b** (2.69, 3.06, 3.88, 4.27, 4.73 Å) [17b] but *p*PEK **3a** had slightly smaller *d*-spacing and peak intensities than those of **3b**. As expected, this reflects a lower degree of crystallinity in *p*PEK **3a** due to the possible presence of 'kinks' arising from ortho-substitution [18a]. Overall, these results are in excellent agreement with the points made based on their thermal behaviors investigated with DSC.

The peak locations (*d*-spacings) between the samples annealed at 190 °C and at 270 °C were slightly different (Fig. 7). The *d*-spacings of the sample annealed at 190 °C are larger than those of the samples annealed at 270 °C. All peak locations from the sample annealed 190 °C are 0.05–0.08 Å larger when compared to those from the sample annealed at 270 °C, which would be evidence of a meta-stable order from annealing at 190 °C.

3.5. FT-IR study of pPEK **3a**

The IR absorption associated with the in-plane bending mode of aromatic C–H is in the range of 1225–950 cm^{-1} in the solid state. Both samples, namely the as-synthesized *p*PEK **3a**, and **3a** annealed at 190 °C, displayed the IBM absorption bands of aromatic C–H bond at 952 cm^{-1} (Fig. 8a). As the annealing temperatures were elevated to 230 and 270 °C, the peak location shifted to a higher frequency at 960 cm^{-1}. The overall peak intensities, however, became gradually weaker as the annealing temperature was increased.

The carbonyl absorption band of an aromatic ketone is in the range 1655–1675 cm^{-1} in the solid state. However, in

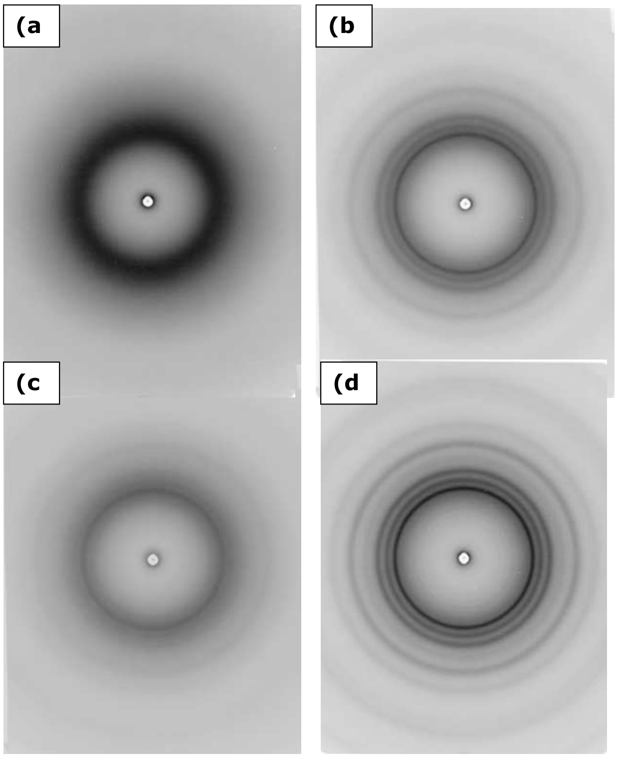


Fig. 6. WAXD patterns for **3a** after subjected to various annealing temperatures: (a) as-synthesized **3a**; (b) 190 °C, 24 h; (c) 230 °C, 24 h; (d) 270 °C, 24 h.

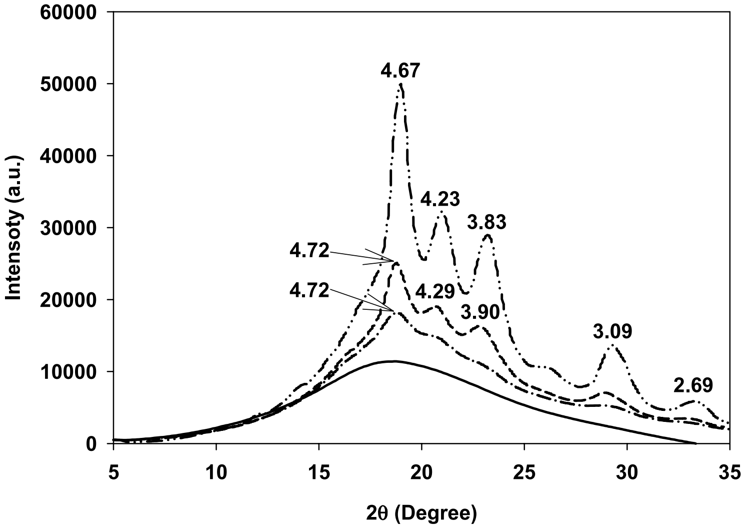


Fig. 7. WAXD curves for **3a** after subjected to various annealing temperatures: (a) as-synthesized **3a** (solid line); (b) 190 °C, 24 h (dash); (c) 230 °C, 24 h (dash-dot-dash); (d) 270 °C, 24 h (dash-dot-dot-dash).

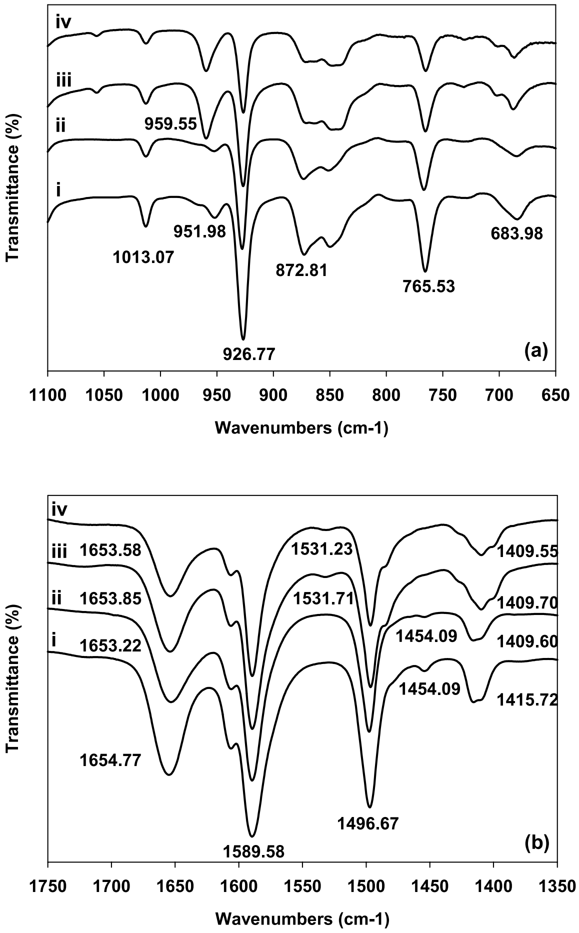


Fig. 8. FT-IR spectra (KBr) of *p*PEK **3a**: (a) 650–1100 cm^{-1}; (b) 1350–1750 cm^{-1}: (i) as-synthesized **3a**; (ii) 190 °C, 24 h; (iii) 230 °C, 24 h; (iv) 270 °C, 24 h.

the structures where the degree of intermolecular interaction is maximized, the carbonyl absorption occurs near 1650 cm^{-1} [23]. The FT-IR spectra of samples annealed at different temperatures contained strong carbonyl absorption bands at the following locations: 1655 (not heat-treated), 1653 (190 °C), 1654 (230 °C), and 1654 cm^{-1} (270 °C). Thus there was essentially no change in the carbonyl absorption frequency despite the differences in annealing temperatures (Fig. 8b). However, the intensities of peaks generally decreased, noteworthy are the bands at 684, 766, 873, 952, 960, 1416, and 1497 cm^{-1} as the annealing temperature was increased.

Although the changes in the IR spectra were small, it is significant that the temperature range (190–270 °C) in which these changes were perceptible coincided with that where the thermal relaxation ($\sim$180–210 °C) and recrystallization ($>$250 °C) processes for *p*PEK **3a** were observed in the DSC and WAXD studies.

4. Conclusion

Our work firmly suggests that an optimized mixture of polyphosphoric acid and P_2O_5 is not only an effective medium that is versatile in playing the roles of solvent, Friedel–Crafts catalyst, and dehydration agent for the synthesis of moderate-to-high MW aromatic poly(ether-ketones), but also possesses an interesting capability related to its viscous nature and the dynamic shear field during polymerization process. Such capability can assert an important influence on the polymer morphology during the polymer-forming and isolation (work-up) stages of either an inherently amorphous or a semi-crystalline polymer, as evidenced by both types of PEKs investigated in this work. We hypothesize that the fundamental basis for this feature is the strain that is imparted to the growing macromolecules by the shear field (generated by mechanically stirring) and 'kinetically stored' because of the viscosity-imposed confinement of macromolecular domains. This stored strain energy that is greater in the case of a semi-crystalline polymer helps to significantly lower the enthalpic requirement for the eventual macromolecular realignment and/or ordering to more thermodynamically stable morphology. Thus, the important contribution of this stored strain energy is to substantially lower the solventless-processing temperature of semi-crystalline polymers. This is illustrated by the compression molding of poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene) or *p*PEK in the temperature range of 230–250 °C that is more than 100 °C lower than its melting temperature. Finally, we should point out that since the molecular weight is directly related to the quantity of such kinetically stored strain, it could be an important factor in determining the occurrence of this unusual thermal behavior observed in this work. Furthermore, our work indicates that this thermal phenomenon has occurred for the range of relatively high molecular weights as reflected in the corresponding intrinsic viscosity values, 0.64–2.10 dL/g. Nevertheless, we are uncertain at this point what the MW threshold is for the phenomenon to take place.

References

[1] (a) Fried JR. In: Mark JE, editor. Polymer data handbook. New York: Oxford University Press; 1999. p. 479.
  (b) Madkour TM. In: Mark JE, editor. Polymer data handbook. New York: Oxford University Press; 1999. p. 480.
  (c) Teasley MF, Hsiao BS. Macromolecules 1996;29:6432 and references therein.
  (d) Wood AS. Mod Plast Int:88.
[2] Bonner, WH. US Patent 3 065 205; 1962.
[3] Dahl, K. US Patent 3 953 400; 1976.
[4] Marks, BM. US Patent 3 441 538; 1969.
[5] Colquhoun HM, Lewis DF. Polymer 1988;29:1902.
[6] Niume K, Toda F, Uno K, Hasegawa M, Iwakura Y. J Polym Sci A, Polym Chem 1982;20:1965.
[7] Sweeney W. Eur Pat Appl 1988;254431.
[8] Johnson RN, Farnham AG, Clendinning RA, Hale WF, Merriam CN. J Polym Sci A1 1967;5:2375.
[9] Radlmann VE, Schmidt W, Nischk GE. Makromol Chem 1969;130:45.
[10] (a) Baek JB, Tan LS. Polymer 2003;44:4135.
  (b) Baek JB, Tan LS. Polym Prepr 2002;43(1):533.
[11] (a) Baek JB, Juhl SB, Lyons CB, Farmer BL, Tan LS. Polym Prepr 2002;43(2):1130.
  (b) Baek JB, Lyons CB, Tan LS. Polym Prepr 2003;44(1):825.
[12] Baek JB, Tan LS. Polym Prepr 2002;43(1):514.
[13] (a) Baek JB, Lyons CB, Tan LS. Polym Prepr 2003;44(1):925.
  (b) Baek JB, Lyons CB, Tan LS. J Mater Chem 2004;14:2052.
[14] Baek JB, Lyons CB, Tan LS. Macromolecules 2004;37:8278.
[15] Baek JB, Price GE, Lyons CB, Tan LS. Polym Prepr 2003;44(2):914.
[16] Eaton PE, Carlson GR, Lee JT. J Org Chem 1973;23:4071.
[17] (a) Attwood TE, Dawson PC, Freeman JL, Hoy LR, Rose JB, Staniland PA. Polymer 1981;22:1096.
  (b) Baek JB, Tan LS. Polymer 2003;44:3451.
  (c) Baek JB, Tan LS. Polym Prepr 2001;42(2):468.
[18] (a) Ueda M, Sato M. Macromolecules 1987;20:2675.
  (b) Ueda M, Kano T. Makromol Chem, Rapid Commun 1985;5:833.
  (c) Kirk BA, Carran MA, Feld WA. Polym Prepr 1991;31:455.
[19] Since the unusual thermal relaxation phenomenon was only observed for the polymers prepared in PPA/P_2O_5 medium, for simplification we purposely kept constant the concentration of all monomers at 5 wt % (the concentration of the resulting polymer should be lower than 5 wt % due to the loss of water as by-product for each repeat unit).
[20] We found that the polymerization dope at 100 °C had had enough leg that a fiber with a diameter of approximately 400 μm (0.4 mm) could be drawn with just the force of gravity, and we felt that the fiber diameter should be controllable with the control of spinning rate. Systematic fiber spinning and characterization studies are currently underway.
[21] In Scheme 2, the strained and relaxed states of PEKs were pictorially represented by the oval and circular domains, respectively. We believe that their morphological difference should be discernable with SEM and related techniques. This is part of the follow-on work that is currently underway.
[22] It was reported that pPEK that is structurally identical to **3a** and **3b** but was prepared using PPMA as condensing agent and solvent could achieved an inherent viscosity up to 0.32 dL/g (measured at 0.5 dL/g; 30 °C; conc. H_2SO_4). No T_g was detected by DSC, but a T_m was observed at 369 °C that is higher than either **3a** (344 °C) or **3b** (361 °C). The fact that its T_m is closer to **3b** seems to imply that a higher degree of para-substitution under PPMA conditions. See Ueda M, Oda M. Polym J (Japan) 1989;21:673.
[23] Silverstein RM, Bassler GC, Morrill TC. Spectrometric identification of organic compounds. 4th ed. New York: Wiley; 1980, p. 124.