

High glass transitions of high-performance thermoplastics¹

M.Y. Keating*

Du Pont de Nemours and Company, Central Research and Development Experimental Station, Wilmington DE 19880, USA

Received 8 June 1998; received in revised form 8 June 1998; accepted 12 June 1998

Abstract

Demand of high-performance engineering thermoplastics in industrial countries drives the development of this class of materials in over 30 years. They display high heat distortion temperature, high modulus and strength, dimensional stability, chemical resistance, inherent flame retardancy and share the commonality of high glass transition. The observed variations of T_g with composition are compared with the postulated using Van Krevelen's structural group contribution theory. The predicted T_g does not differentiate the variations affected by moisture and crystallinity. The 'wet' T_g 's are determined by modulated temperature-DSC (MT-DSC), while the 'dry' or the constrained T_g due to orientation and/or annealing is detectable by standard DSC. The glass transitions of the constrained domains in highly crystalline polymers can be followed by DMA, DEA and thermal expansibility. © 1998 Elsevier Science B.V.

Keywords: High-performance polymers; Van Krevelen's group contribution theory; Dry T_g ; Wet T_g ; Constrained T_g

1. Introduction

A class of high-priced, low-volume, high-performance engineering polymers, which represent only about 0.1% of the volume of thermoplastics sold today in USA were commercialized in the 1970s and 1980s. They are polyesters, polyamides, polyimides, polysulfides, polyetherketones, polyethersulfones, polyetherimides. Thermotropic liquid crystal polymers gain attention since mid-1980s and 1990s. The commonality of this class of high-performance polymers are the high glass transition temperatures and most are moldable. Their heat distortion temperatures (HDT) are at 170–355°C and their selling price is at US\$ 5–100 per kg. Their stringent property specifications for

special applications include (a) high chemical, hydrolytic, radiation and abrasion resistance, (b) precise, stable, reproducible dimensions, (c) inherent flame retardancy, (d) high HDT and thermal cut-through temperatures, (e) cryogenic stability, (f) low dielectric constant, high dielectric breakdown strength, (g) affinity to reinforcement, and (h) color coding and printing. The latest growth phase in 1990s is not in material discovery but in extensive applications in health care, aerospace, automotive, electronic industries, which include microwavable foodwares and bags, surgical and dental tools, dialysis membranes, as well as aircraft interiors, electrical connectors, integrated circuit chip carriers, computer casings and disks. More detailed markets and applications can be found in the special reports [1,2].

The high-performance polymers can be amorphous or semi-crystalline, and are almost all aromatic rigid hydrocarbons between the links of functional groups.

*Corresponding author.

¹Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday.

The glass transition is an important property which determines lower usage temperatures while the crystalline melting transitions limit the upper service temperature. The glass transitions have strong correlations with their chemical structures and can be estimated from Van Krevelen's group contribution theory [3]. In their work on prediction of glass transition from structure, Van Krevelen and Hoftyzer believed that the product $T_g M$ behaves as an additive function, which was called the molar glass transition function, Y_g (K kg mol^{-1}). The Y_{gi} of the relevant unit in the structure depends also on its neighboring groups. The aromatic ring units have weight fractions higher than the aliphatic atoms. Thus, the resulting glass transition temperatures of this class of materials are high.

The predicted glass transitions are not always close to the measured values. We know that the glass transition varies not only with the composition, but also with the moisture content and degree of crystallinity. The process and thermal histories are important, if and when the glass transition temperatures are cited. Some polymers can absorb up to a few percentage of moisture at the polar functionality; this plasticizes the long-range motion of the polymer chains and lowers the relaxation temperature. Some polymers are slow of crystal packing in the crystallization process which leave the polymers semi-amorphous if not fully amor-

phous. Careful attention must be paid to the processes used.

2. Materials and experimental

This paper is not intended to be a survey of high-performance thermoplastics in the world market, but a compilation of the high glass transition materials and their measurement that our laboratory has carried out. Half of these are semi-crystalline and the other half are amorphous. The high glass transition materials along with their chemical abbreviations and sources from where we purchased are listed in Table 1. The chemical structures will be given in Section 3. Most contain glass fillers. Polyethylene terephthalate (PET) does not meet the stringent requirements of properties and is not a high-performance thermoplastic, but rather a mid-volume commodity polymer. It is included here for benchmarking the glass transition temperatures and other properties. The T_g of PET is predicted by Van Krevelen at 351 K (or 78°C) [3], while the wet T_g measured by modulated temperature-DSC (MT-DSC) of the specimen at normal storage condition is 70°C, the dry T_g is 80°C, the oriented and heat set T_g is as high as 90°C. The UL[®] continuous service temperature index for PET is high at 150°C for a commodity polymer. Included also in this paper are the conventional polyimide Kapton[®] 100H which is a

Table 1
Material chemical abbreviations and suppliers

Polymer	Chemical name	Supplier
PET	Polyethylene terephthalate	DuPont Company
PPS Ryton [®] R-4	Polyphenylene sulfide	Phillips petroleum
SPS	Syndiotactic polystyrene	Dow Chemical
HTN Zytel [®] 501	High-temperature nylon 6T/DT 50/50	DuPont Company
Arlen C2000	High-temperature nylon 6T/66 55/45	Mitsui Petrochemical
PEN	Polyethylene naphthalate	Eastman Chemical
PEKK Declar [®]	Polyetherketoneketone	DuPont Company
PEEK Victrex [®]	Polyetheretherketone	Victrex plc
PC Laxan [®]	Polycarbonate	General Electric
PES Victrex [®]	Polyethersulfone	Sumitomo Chemicals
PES Udel [®]	Polyethersulfone	Amoco Corporation
PES Radel [®]	Polyethersulfone	Amoco Corporation
LCP Zenite [™] 6130	Liquid crystal polymer	DuPont Company
LCP Vectra [®] A130	Liquid crystal polymer	Hoechst Celanese
LCP Xydar [®] G330	Liquid crystal polymer	Amoco Corporation
Kapton [®]	Oxydianiline pyromellitimide	DuPont Company
Nomex [®] T-430	Meta-phenylene isophthalamide	DuPont Company
Kevlar [®] 49	Para-phenylene terephthalamide	DuPont Company

thermoset rather than thermoplastic, and liquid crystal polymer Kevlar[®] 49 which is lyotropic rather than thermotropic polymers. These materials are top-of-the-line unique high performers with a continuous service temperature index above 400°C.

2.1. 'Dry' and 'wet' glass transitions of the amorphous region

To remove the absorbed moisture, the polymer was heated in TA Instruments 2920 DSC to 30°C above the melting point under nitrogen blanket, quench cooled to a temperature below the glass transition by removing it from heating source immediately and reheated again from ambient temperature to 30°C above melting at 10°C min⁻¹ rate. The glass transition from this second cycle heating is the 'dry' T_g . The glass transition at its normal storage state, which may have absorbed moisture, was measured in TA Instruments 2920 modulated temperature-DSC by heating from ambient temperature to 30°C above the melting point at the rate of 3°C min⁻¹ with oscillation amplitude of $\pm 0.637^\circ\text{C}$ and period of 80 s under nitrogen blanket. In both methods, calibration was carried out using the melting points of indium, tin and zinc at appropriate heating rates. There would be some degree of drying in DSC before reaching the glass transition. The T_g measured in MT-DSC method is lower than that taken after quenching from melt state. The 'wet' glass transition, much higher than the boiling point of water cannot be determined by thermal constant heating rate methods.

2.2. Glass transition of the constrained region

The chain motion in the amorphous region of a fully crystallized or mechanically oriented semi-crystalline polymer is somewhat restricted being adjacent to the crystal face. The glass transition corresponding to the constrained motion of this amorphous region is smaller in magnitude than can be detected by the MT-DSC method described above or by dynamic mechanical analysis (DMA) below.

2.3. Isothermal crystallization

The entire crystallization rate (inverted $t_{1/2}$ of isothermic crystallization exothermic peak) vs. tempera-

ture curve was determined by isothermal method. For the crystallization rate from melt state, 10 mg of specimen was heated at 50°C min⁻¹ to 30°C above melting point in Perkin-Elmer DSC7, held there for 3 min till it was melted and then cooled rapidly at 200°C min⁻¹ to crystallization range and held there till completion. For the crystallization rate from the amorphous state, the specimen was first melted and quenched cooled to liquid nitrogen temperature. The quenched specimen was then heated from 30°C below glass transition temperature to crystallization range at 200°C min⁻¹ and held there till completion.

2.4. Dynamic mechanical analysis

Film or fiber specimen was measured in Seiko Instruments 210 DMS tensile mode in multiple frequencies (1, 2, 3, 5, 10, 20 Hz) at the heating rate of 2°C min⁻¹ of entire temperature of interest. Initial force was set at 200–800 g and automatically attenuated to a base force of 0.5 N (50 g) at higher temperatures; the oscillation amplitude was set at 10 μm . The mechanical loss peak taken at 1 Hz in the T_g region is considered as the constrained or 'wet' (if moisture was absorbed) T_g of the film or fiber. The glass transition measured in second cycle of heating was considered the 'dry' T_g . The temperature scale marker was polycarbonate at 148°C with a mechanical loss peak at 1 Hz.

Thicker specimen (3.2 mm) was measured in TA Instruments 983 DMA in bending mode at 3°C min⁻¹ heating rate of the temperature range of interest. The oscillation amplitude was set at 0.7 mm. The glass transition taken in first cycle of heating of a thick specimen can be treated as the 'wet' T_g , because the moisture evaporation from this thickness is slower than the heating rate.

2.5. Thermomechanical analysis

Film or fiber specimen was measured in TA Instruments 2940 TMA in film/fiber mode with force of 0.05 N (5 g) and heating rate of 5°C min⁻¹. The temperature at which a sudden change in the expansion coefficients occur is the glass transition temperature. If this temperature is below the boiling point of water, the glass transition is the 'wet' T_g ; otherwise it is the 'dry' T_g . The T_g taken in second cycle of heating

is always the 'dry' T_g . The temperature scale was calibrated with melting points of indium, tin and zinc wires. The expansion scale was standardized with the expansion coefficient of aluminum wire.

2.6. Dielectric analysis

Carefully wound Kevlar[®] fiber mat, sandwiched between plates in TA Instruments 2970 DEA, was heated from 0°C to 400°C twice in six frequencies (1, 10, 100, 1000, 10 000, 100 000 Hz). The glass transition was taken at tan delta maximum at 1 Hz in the second cycle of heating.

3. Results and discussion

The uniqueness of this class of high-performance thermoplastics is their high glass transition temperatures (T_g), which allow continuous-use temperatures to be high according to UL[®]746B temperature indices. T_g and the characteristic inherent flame retardancy, high heat distortion temperature (HDT) and chemical resistance are attributed to the aromaticity in the backbones and the unique arrangements of these groups. Van Krevelen [3] believes that the chemical structure and molecular weight determine all properties of polymers: the cohesive forces, the packing density and the molecular mobility directly, the morphology and relaxation phenomena indirectly. The molecular weights of these commercial materials studied in this paper are sufficiently high and are not the contributors of the variation of glass transitions. This leaves the chemical structure as the main focus, since there are no blending or diluent involved.

The glass transition is the temperature where a long-range cooperative segmental motion occurs in the amorphous phase in either an amorphous or a semi-crystalline polymer. The basis of glass transition and the its dependency on many factors are discussed intensively in excellent books and publications [4,5], including the most recent books [6,7]. In the following sections dealing with high-performance polymer groups we will give the predicted glass transitions, based on Van Krevelen's group contribution theory of repeating units and the measured glass transitions. The variations of T_g due to moisture in their normal storage conditions and crystallinity will

be also included. A summary of the glass transitions are provided in Table 2.

The process for high-performance thermoplastics are, in complicated part designs, technically sophisticated. The crystallinity of semi-crystalline polymers is an important property. It is essential to determine the process windows and have clear pictures of the range of crystallization temperature in every process. Most poor processes are the result of little understanding of the morphological dynamics as a function of temperature. Heat-induced crystallization affects, during service life of the material, the precise dimensions that are critical in any end use. For those polymers having a narrow window of processing to produce optimum performance, minor variations can seriously compromise the properties. Once the process window is determined, the constrained T_g of a fully crystallized and sometimes oriented polymer becomes clear.

Since the observation by Suzuki et al. [8] of three-phase system in semi-crystalline polymers in 1985, proposals [6,9] and workshops [10–15] can be found useful to distinguish mobile amorphous phase and rigid amorphous fraction. The constrained glass transition here is not the rigid amorphous fraction. The latter is non-crystalline but does not participate in glass transition [11]. The constrained T_g is the mobility-restricted amorphous phase after a secondary crystallization occurs adjacent to the primary crystals due to mechanical or thermal treatment, and is measurable by thermal techniques.

3.1. Polyamides

The high-temperature polyamides (HT-nylon) has excellent physical and electrical properties at high temperatures (in addition to their heat resistance, chemical resistance and abrasion resistance) to be used in electronic connectors, fuse holders and automotive under-the-hood applications. Two HTNs are compared here: DuPont's Zytel[®] 501 (6T/DT 50/50 wt.%) and Mitsui's Arlen C2000 (6T/66 55/45 wt.%). Both are semi-crystalline thermoplastics. Zytel[®] 501 is a copolymer of terephthalic acid and two diamines in 50/50 ratio, hexamethylenediamine and methylpentamethylenediamine; while Arlen C2000 is copolymer of hexamethylenediamine and two diacids in 55/45 ratio, terephthalic acid and adipic acid. With terephthalic acid in every repeating unit

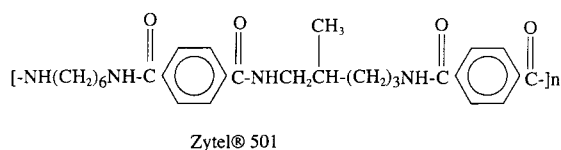
Table 2

High glass transitions of synthetic polymers (the predicted, the measured wet, dry and the constrained)

Polymers	$T_g = \sum_i Y_{gi}/M$ predicted (K)	Wet T_g (°C)	Dry T_g (K) ^a	Constrained T_g (°C)	T_m (°C)	UL [®] T° index (°C)
PET	351 = 67400/192.1	70	353 (80)	85–90	256	150
PPS Ryton R-4	347 = 37500/108.2		361 (88)	93	285	220
SPS	373 = 38800/104.1	91	367 (94)	103	269	
HTN Zytel [®] 501	410 = 101000/246	89	403 (130)	138	301	
HTN Arlen C2000	380 = 90300/237.4	54	351 (78)	84	311	
PEN	414 = 100400/242.2		399 (126)	132–140	266	155
PEEK 150G	421 = 121400/288.3		420 (147)	156–158	356	250
PEKK 100T	473 = 142000/300.3		436 (163)	180	382	
PEKK 80/20 T/I	469 = 140800/300.3		430 (157)		360	
PEKK 70/30 T/I	467 = 142200/300.3		426 (153)	170	333	
PEKK 60/40 T/I	465 = 139600/300.3		429 (156)	175	326	
PC Lexan [®]	421 = 107000/254.3		420 (147)			
PES Victrex [®]	495 = 115000/232.3		501 (228)			190
PES Udel [®]	465 = 206000/442.6		461 (188)			150
PES Radel [®]	472 = 189000/400.5		491 (218)			
PEI Ultem [®] 1000	493 = 285000/578		490 (218)			175
LCP Vectra [®] A130	421 = 193000/410			105 (378 K)		
LCP Zenite [™] 6130	432 = 56300/130.2			105 (378 K)	340	
LCP Xydar [®] G330	412 = 198000/480			112 (385 K)	350	
Kapton [®] 100H	633 = 242000/382.3			360 (633 K)		400
Nomex [®] T-430	470 = 112000/238.3			285 (558 K)		
Kevlar [®] 49	621 = 148000/238.3			330 (603 K)		

^aValues in parenthesis are in °C.

Zytel[®]501 is expected to raise the rigidity of the polymer chains and the glass transition higher than the chains composed of only 0.55% of terephthalic acid and 0.45% of adipic acid in Arlen C2000. The presence of 50% of the branched methylpentamethylenediamine segment in Zytel[®]501 has complications on the crystal packing and crystallization rate [16,17] and has an impact on the chain motion in amorphous region, when compared to linear hexamethylenediamine segment in both HTNs.



The glass transitions are estimated following Van

Krevelen's molar glass transition function Y_g :

$$T_g = \frac{Y_g}{M} = \frac{\sum_i Y_{gi}}{\sum_i M_i}$$

For Zytel[®]501, a 6T/DT 50/50 mol % copolyamide, the calculations are

$$Y_g = Y_g(\text{COC}_6\text{H}_4\text{CO}) + 2 \times Y_g(\text{NH}) + 0.5 \times 6 \times Y_g(\text{CH}_2) + 0.5 \times 4 \times Y_g(\text{CH}_2) + 0.5 \times Y_g(\text{CH}-\text{CH}_3) = 62 + 2 \times 7 + 0.5 \times 10 \times 4.3 + 0.5 \times 8 = 101.5$$

$$M = (\text{COC}_6\text{H}_4\text{CO}) + 2 \times M(\text{NH}) + 0.5 \times 6 \times M(\text{CH}_2) + 0.5 \times 4 \times M(\text{CH}_2) + 0.5M(\text{CH}-\text{CH}_3) = 246.1$$

$$T_g = 101 \times 1000/246 = 411 \text{ K}$$

For Arlen C2000, a 6T/66 57/43 mol % copolyamide, the calculations are

$$\begin{aligned}
 Y_g &= 0.57 \times Y_g(\text{COC}_6\text{H}_4\text{CO}) + 6 \times Y_g(\text{CH}_2) \\
 &+ 2 \times Y_g(\text{NH}) + 0.43 \times 2 \times Y_g(\text{CO}) \\
 &+ 0.43 \times 4 \times Y_g(\text{CH}_2) = 0.57 \times 62 + 6 \\
 &\times 4.3 + 2 \times 7 + 0.43 \times 2 \times 9 + 0.43 \times 4 \\
 &\times 4.3 = 90.3
 \end{aligned}$$

$$\begin{aligned}
 M &= 0.57 \times M(\text{COC}_6\text{H}_4\text{CO}) + 6 \times M(\text{CH}_2) \\
 &+ 2 \times M(\text{NH}) + 0.43 \times 2 \times M(\text{CO}) \\
 &+ 0.43 \times 4 \times M(\text{CH}_2) = 237
 \end{aligned}$$

$$T_g = 90.3 \times 1000/237.4 = 380 \text{ K}$$

The DSC measurements of dry polyamides were carried out by heating, at first, to 30°C above the melting points. The subsequent scans show clearly the dry T_g 's. The actual measured glass transitions for Zytel[®]501 and Arlen C2000 are $T_g=403 \text{ K}$ (130°C) and $T_g=351 \text{ K}$ (78°C), respectively. Their melting points are $T_m=301^\circ\text{C}$ and $T_m=311^\circ\text{C}$. Polyamides absorb 1–2% percentage of water. The glass transitions of polyamides at the normal storage state were measured in MT-DSC which deconvolutes the glass transition event as the reversible process and shows the wet T_g at 89°C and 54°C for Zytel[®]501 and Arlen C2000. These temperatures are lowered by $T=36^\circ\text{C}$ and 24°C due to the binding of water molecules to the amide functional groups allowing the chain motions to be easier with less interchain hydrogen bonds. The glass transitions of the fully crystallized and annealed Zytel[®] and Arlen C are 138°C and 84°C. These temperatures are raised by $T=13^\circ\text{C}$ and 6°C due to additional crystallization at the expense of amorphous domain on the surface of the primary crystals which restricts the chain motions between the lamellar crystal layers. A composite plot of T_g variations of Zytel[®]501 is given in Fig. 1.

The process windows of Zytel[®]501 and Arlen C2000 were studied. These process windows, expressed the isothermal crystallization rates (s^{-1}) in the temperature window, are helpful to produce fully crystalline polyamides. See Fig. 2. They provide the correct mold temperatures to produce dimensional stable parts. Outside the crystallization range, the molded parts are amorphous which affect the dimensional stability during the service life. The fastest crystallization temperatures estimated from the curve maxima are 215°C and 190°C for Zytel[®]501 and

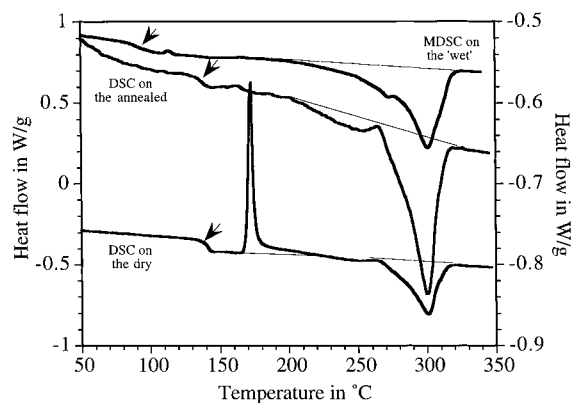


Fig. 1. DSC scans of high-temperature polyamide Zytel[®]501: top is the MT-DSC curve on sample at normal storage condition, bottom is the DSC curve on quenched sample, middle is on annealed sample at 220°C.

Arlen C2000. The fastest crystallization rates of Arlen C are not measurable by DSC.

3.2. Polyphenylene sulfide

Polyphenylene sulfide Ryton[®] R4 is a semi-crystalline linear polymer from Phillips Petroleum. The PPS of uncluttered benzene ring and simple sulfur bonds in para position exhibits high temperature stability, inherent flame retardancy and good chemical, abrasion resistance. The high glass transition and high crystallinity allow the molded parts to be reproducible

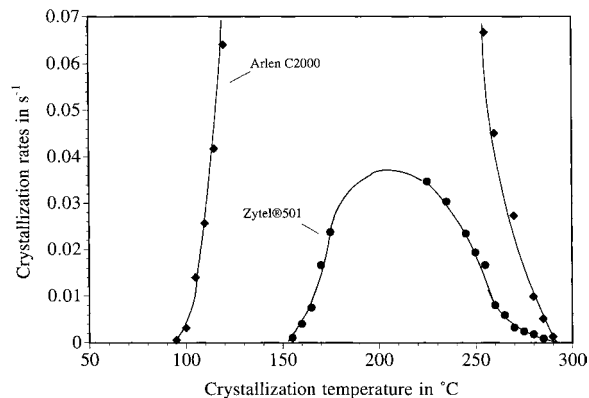
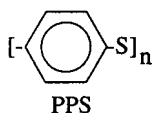


Fig. 2. DSC isothermal crystallization rates of polyamides Zytel[®]501 (circles) and Arlen C2000 (diamonds). The rate maxima are at 215° and 190°C, respectively.

and uniform even at high temperature. It is used in most aggressive chemical environments and high temperature requirements. PPS does not absorb water; thus there is no wet T_g . The predicted glass transition based on Van Krevelen's equation is 347 K (74°C); the actual measured dry T_g from rapid quenching DSC method is 361 K (88°C). The melting point is 285°C. T_g and T_m agree with Cheung's data [18]. PPS Ryton[®] R-4, the glass reinforced resin, crystallization very fast. According to Phillips' literature, it can approach maximum crystallinity if mold is hotter than 121°C. Crystallizing at 135–150°C, it takes just 20% more time (3–5 s). The glass transition of fully crystallized and annealed is 366 K (93°C). See Table 2.



3.3. Syndiotactic polystyrene

The metallocene technology has made the commonly known atactic polystyrene into high-performance semi-crystalline thermoplastics. The tacticity of the repeating units are highly ordered in an alternating configuration. It exhibits good heat and chemical resistance, electric property, dimensional stability, and is insensitive to moisture. It can be used in automotive under-the-hood components, electronic parts and where heat and chemical resistance is required. The predicted T_g from Van Krevelen's equation is 373 K (or 100°C). The actually measured T_g from quenched sample is 94°C. Although it is not moisture sensitive, the T_g measured by modulated DSC is slightly lower at 91°C. The difference is not as large as seen in polyamides. See Table 2. The fully crystallized and oriented sample shows a constrained T_g in much smaller magnitude in DSC at 103°C. The three glass transitions are compared in the DSC scans in Fig. 3. The crystallization rates of SPS in 1 s^{-1} are given in Fig. 4 where the fastest rate is estimated at 185°C. The mold temperature outside the crystallization range would result in amorphous parts.

3.4. Polyetherketones

The family of polyetherketones studied are semi-crystalline thermoplastics: Victrex plc's PEKK[™]

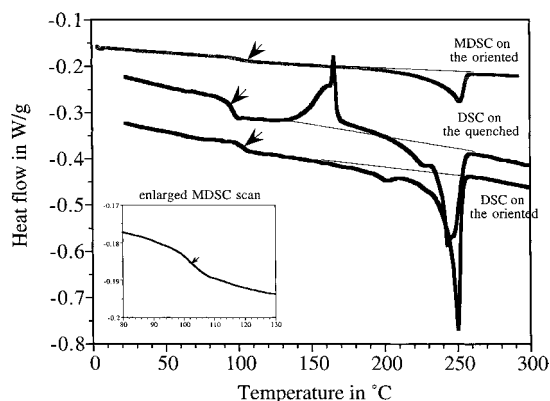


Fig. 3. DSC scans of syndiotactic PS: top is the MT-DSC curve on sample at normal storage condition, middle is the DSC curve on quenched sample, bottom curve is on the biaxially oriented film.

150G (previously ICI's) and DuPont's PEKK Declar[®]s. Like other families of high-temperature thermoplastics, they have good high continuous-use temperature, inherent flame retardancy, high dimensional stability, high chemical, hydrolytic and radiation resistance, high dielectric breakdown strength for insulating usage. Polyetherketones are highly desirable in automotive, electronic, industrial and medical applications. PEKK Declar[®]s produce low level of smoke and resist combustion which are the choice for aircraft interiors. Review article by Rao [19] on amorphous and crystalline polyetherketones covers many variations of polyetherketones. Other more

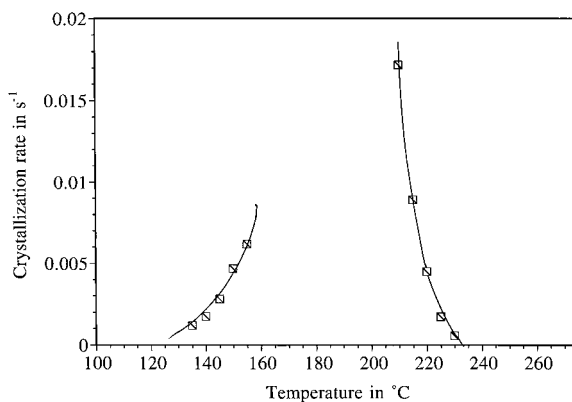
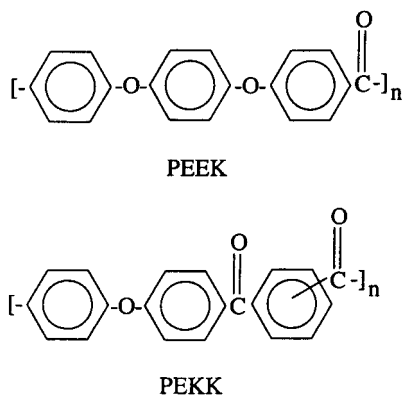


Fig. 4. DSC isothermal crystallization rates of syndiotactic-polystyrene. The rate maximum is at 185°C.

exotic versions of polyetherketoneimides, polyetherketonesulfones, polyetherketoneamides [19] and poly(phenylenethioetheretherketone)s [20] are the further possibilities.



PEKK Declar[®]s show a wide range of crystallinities by replacing a fraction of the para-ketone with meta-ketone. The glass transitions change only slightly with it. However, the estimated T_g using Van Krevelen's contributing Y_{gi} , selected from the best choices of grouping, are 35–40°C higher the measured. The measured dry glass transitions from quenched DSC method are 163°C, 157°C, 153°C, 156°C for PEKK 100T, 80/20 T/I, 70/30 T/I, 60/40 T/I, respectively. All are slightly higher than PEEK 150G, which shows a dry T_g at 147°C. The difference between PEKK 100T and PEEK is 16°C. The T_g of the fully crystallized and annealed PEEK and PEKKs are 10–20°C higher than the appropriate quenched dry samples. See Table 2.

Changing the ratios of ether/ketone and para-/meta-ketone in polyetherketones affect the crystallization rates much more severe than the glass transitions. The fastest crystallization temperatures of PEEK 150G, PEKK 100T and PEKK 70/30 T/I are shifted too; this agrees with the shifts seen in T_g . As shown in Fig. 5, the crystallization rates of PEEK and PEKK 100T are both fast, although PEKK 100T requires high process temperature to be equivalent. The fastest crystallization temperatures are estimated to be 235°C and 255°C for PEEK and PEKK 100T, respectively. The rates at the fastest crystallization temperatures are not measurable by DSC. The amount of shifts are also reflected in the 16°C difference found in glass transition temperatures. Crystallization of meta-ketone con-

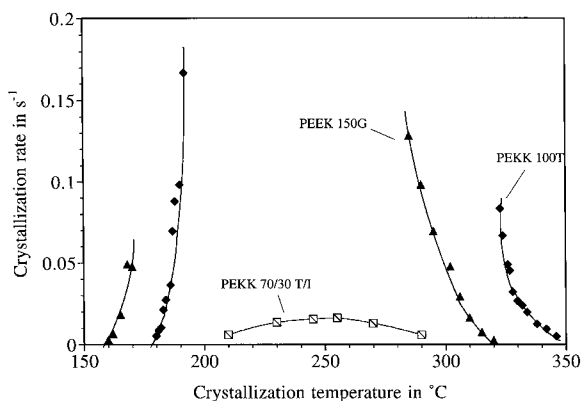


Fig. 5. DSC isothermal crystallization rates of polyetherketones: PEKK 100T (diamonds), PEEK Victrex[®] 150G (triangles), PEKK 70/30 T/I (squares). The rate maxima are at 255°C, 235°C and 255°C, respectively.

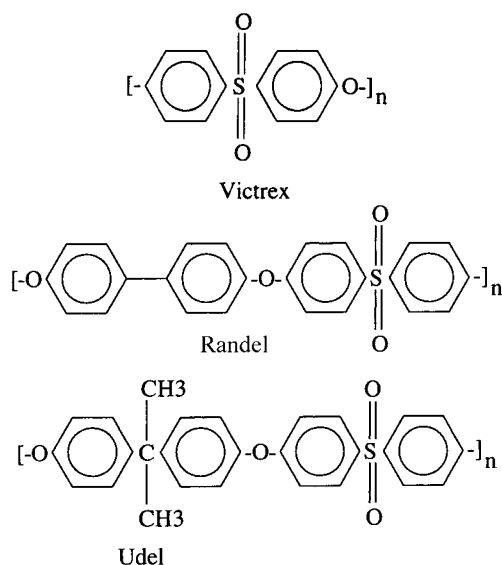
taining polymers are expected to be slow. PEKK 60/40 is an amorphous material and can be crystalline after annealing, while 70/30 is slow crystallizing with the fastest rate being only 0.017 s⁻¹ at 255°C.

3.5. Polyethersulfones

Polyethersulfones from three sources are compared: Sumitomo Chemicals' Victrex[®], Amoco Corporation's Udel[®] and Randel[®]. They are all amorphous polymers. The PES is approved by USDA and FDA for the use in food contact and medical tools due to their ability to withstand repeated steam sterilization and detergents. Other desirable properties include high heat distortion temperature, chemical resistance, long-term dimensional stability, inherent flame retardance and suitability for electrical applications.

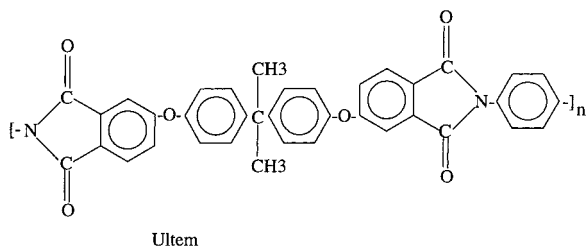
The Sumitomo Chemicals' Victrex[®] (previously ICI's) has highest glass transition of the three PES at 228°C with simpler structure of alternating ether and sulfone linkages between benzene rings. The T_g predicted from Van Krevelen's group contribution is 495 K (or 222°C). The simple ether linkage is replaced by 4,4'-biphenol in Randel[®] and bisphenol-A in Udel[®]. The T_g 's of Amoco's Randel[®] and Udel[®] are measured at 218°C and 185°C, respectively. The predicted T_g 's are slightly higher, as shown in Table 2. From composition viewpoint, the more complicated the component structure, the lower the glass transition.

The T_g 's are readily measurable by DSC method. One of the examples is shown in Fig. 6.



3.6. Polyetherimides

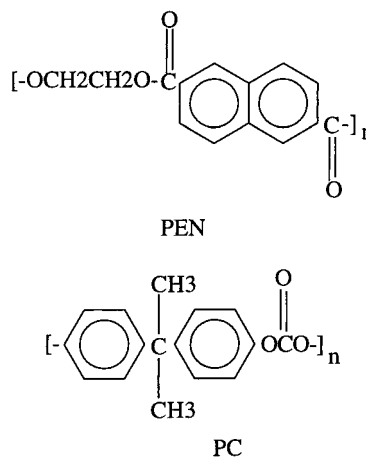
General Electric's Ultem introduced in 1982 is an amorphous polymer made from bisphenol-A, phthalic hydride, methylamine and *m*-phenylenediamine. Although Ultem dominates the market, other structures have been explored by Davies et al. [21]. Ultem's easy processability, chemical and hydrolytic resistance, and low coefficient of expansion are sold in automotive engine components, printed circuit boards and cookwares. PEI 1000 has a glass transition of 218°C. The predicted T_g is 493 K (or 220°C). The glass transition is readily measurable by DSC (see Fig. 6). The continuous service temperature is 175°C.



3.7. Polyesters

Polyethylene naphthalate (PEN) and polycarbonate (PC) in films can be considered as high performance.

The PEN film, also a semi-crystalline polymer, properties are better than those of traditional PET films in the area of heat, chemical, UV, hydrolytic resistance and oxygen barrier. The glass transition measured by quenching from melt in a DSC is 126°C, while the T_g of the biaxially oriented and heat-set film is as high as 140°C. The predicted T_g from Van Krevelen's equation is 414 K (or 141°C). PEN can absorb 0.4% of moisture at 97% RH. The continuous service temperature by UL[®] 746B index is 155°C. See Table 2. PEN crystallizes slowly. It is even slower than HTN Zytel[®] 501 and PEKK (70:30) discussed earlier. The fast crystallization temperature occurs at 210°C with a rate of 0.007 s⁻¹ as shown in Fig. 7. General Electric's bisphenol-A polycarbonate Lexan is an amorphous polymer. It is used in automotive and industrial instrument panels, medical packaging due to its high resistance to steam and dry heat, γ and electron beams [22]. The glass transition can be seen easily by DSC and DMA at 147°C which is close to predicted T_g of 421 K (or 148°C). The DSC measurement of T_g is given in Fig. 6. PC can crystallize with long annealing time to low degree of crystallinity.



3.8. LCPs

Thermotropic liquid crystal polymers (LCPs) are aromatic copolyesters. LCPs are densely packed rod-like polymer chains with unique uni-directional mechanical properties. LCPs are excellent in radiation, hydrolytic, chemical resistance, and have inherent flame retardancy with low smoke, low expansion coefficient. Hoechst-Celanese Corp.'s Vectra[®] A130,

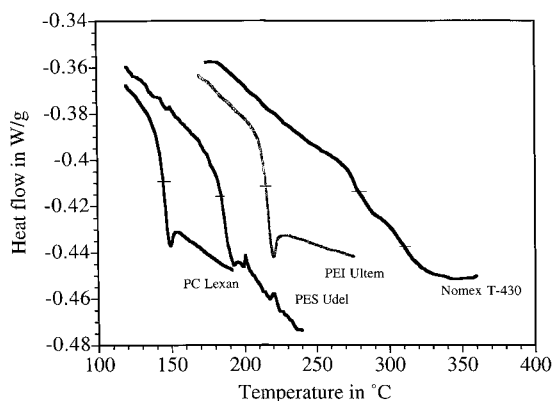


Fig. 6. Glass transitions of amorphous high-performance polymers by DSC: polycarbonate (Lexan[®]), polyethersulfone (Udel[®]), polyetherimide (Ultem[®]), poly *m*-phenylene isophthalamide (Nomex[®]).

DuPont's Zenite[®] 6130 and Amoco Corporation's Xydar G330 are among this type. LCPs are used in automotive under-the-hood parts, actuator motor for cruise controls and electronic, industrial applications where chemical resistance, high temperature stability and high strength are required. The unique parallel alignment of rod-like polymer chains is preserved in their solid state as high orientation which makes its glass transition less conventional. T_g can be detectable by more sensitive methods, e.g., dynamic mechanical and dielectric thermal analyses. Vectra[®] A is made by condensation of 6-hydroxy-2-naphthoic acid and *p*-hydroxybenzoic acid in 27/73 mol % [22]. The predicted T_g from Van Krevelen's group contribution from all components is 421 K (or 148°C). The DMA α transition in its tan delta curve is believed to be the glass transition of 105°C. Xydar G330, a 30% glass filled LCP, is made from 4,4'-biphenol, terephthalic acid and *p*-hydroxybenzoic acid (1:1:2). The predicted T_g is 412 K (or 139°C), while the DMA α peak is seen at 112°C. DuPont's Zenite[®] 6130 is a 30% glass filled LCP of 4,4'-biphenol, hydroquinone, terephthalic acid, 2,6-naphthalic acid, *p*-hydroxybenzoic acid (5:5:7:3:32). The predicted T_g is substantial higher like the other LCPs at 432 K (or 159°C); the DMA α peak is at 105°C. The mechanical tan delta curves of these LCPs are given in Fig. 8.

The lyotropic LCPs of Kevlar[®] and Nomex[®] are aromatic polyamides. They decompose before

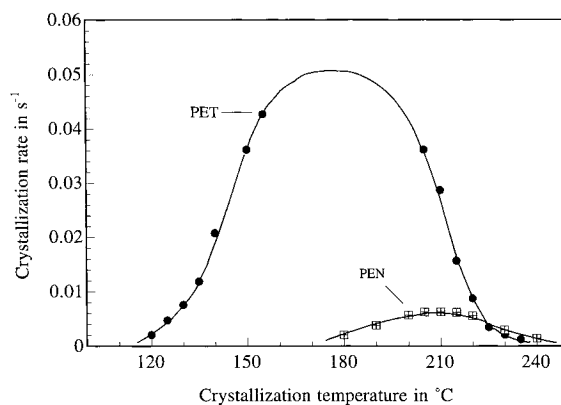


Fig. 7. DSC isothermal crystallization rates of polyesters: polyethylene terephthalate (circles), polyethylene naphthalate (squares). The rate maxima are at 180°C and 210°C, respectively.

melting, and therefore, can only be processed in solution. The Kevlar[®] fibers' high temperature, high modulus and high tenacity properties are well known; it has been used widely in bullet-proof vest, and many other reinforcements where weight, strength and long wear are required, e.g. in boats, in bicycle frames, in tires. The predicted glass transition from Van Krevelen's equation is 621 K (or 348°C). The highly ordered *p*-phenylene terephthamide shows minor disorder region between the rod-like aligned liquid crystals, which is difficult to detect by DSC. In Fig. 9, the sudden shrinkage of single Kevlar[®] 49 fiber at 330°C marks the glass transition where the non-crystalline stretched chain starts to relax. The dielectric tan delta signal at 1 Hz showed a maximum at 330°C where the Kevlar[®] fiber mat was heated in DEA (Fig. 9). Kevlar[®] 49 can absorb 6% of moisture at 97% RH. Nomex[®] can be made in papers or fibers. Its unique high temperature, heat insulation and no-burn properties are utilized in firemen's garments, and heat insulating gloves. The glass transition of Nomex[®] T-430 is predicted at 470 K (or 197°C) based on its meta substitution of amide groups on the benzene rings. However, the measured T_g by DSC (Fig. 6) and DMA are much higher at 285°C. The stiffness and alignment of Nomex[®] chains may be the cause of the difference; we believe that T_g is constrained between the liquid crystals. See Table 2.

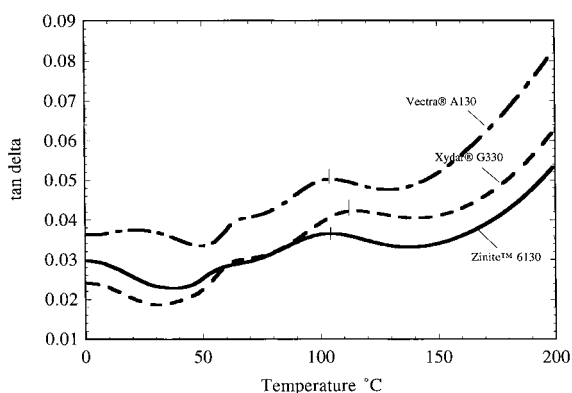
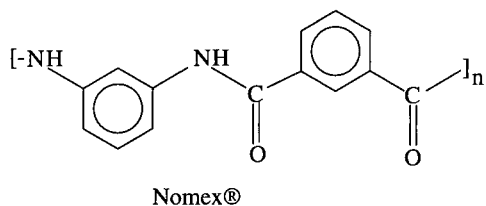
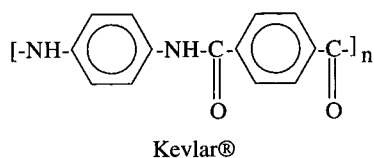
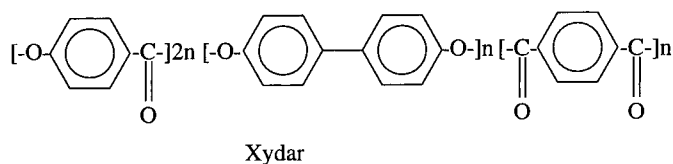
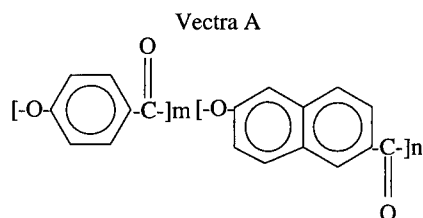


Fig. 8. DMA tan delta signals of the glass filled liquid crystal polymers: Zenite[®] 6130, Vectra[®] A130 and Xydar[®] G330. The glass transitions are marked..



3.9. Polyimides

Kapton[®] H and Vespel[®] SP are high temperature thermosetting polymers of oxydianiline and pyromel-

itic dianhydride sold in films and compacted structures, respectively. The polyimides are known for their high-temperature and low-temperature stability. The continuous-use temperature is tested as high as 400°C for Kapton[®]. The other excellent properties include wear, electrical, chemical and radiation resistance, flame retardancy and low thermal conductivity. The principal use of Kapton[®] films is in electronic insulations and flexible connectors. The metalized Kapton[®] is being used in space vehicles, solar cells and cryogenic storage tanks. The same excellent property of Vespel[®] is utilized in electronic and computer industries. The predicted T_g is at 633 K (or 360°C) according to Van Krevelen's group contribution theory. The actual measured T_g is 360°C by DMA and DEA. Kapton[®] 1/1000 inch film can absorb 3% moisture at 97% RH.

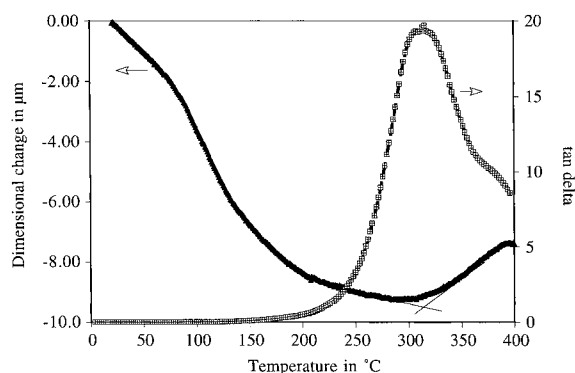
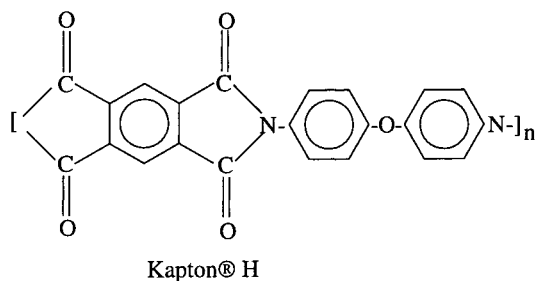


Fig. 9. Glass transition of poly(*p*-phenylene) terephthalamide Kevlar[®] 49 fiber by dimensional change and DEA tan delta curve maximum.



4. Conclusion

High-performance engineering polymers share the commonality of aromaticity between the functional groups and high glass transitions. The glass transition can be predicted reasonably close by Van Krevelen's group contribution theory. The simple and symmetric structures tend to be crystalline and relatively higher T_g , whereas the complicated asymmetric structures are amorphous and relatively lower T_g . The asymmetry can slow down the crystallization rate to an extent that they stay amorphous. Moisture lowers the glass transition temperatures, but the wet T_g are not always measurable for these temperatures are higher than the boiling point of water. Mechanical and thermal treatments raise the crystallinity, thus restrict the long-range motion in mobile amorphous phase and T_g 's are higher.

References

- [1] E.A. Cleaver, T. Schellenberg, Y. Sakuma, *Liquid Crystal Polymers, Specialty Plastics*, 580.4200A in *Chemical Economics Handbook*, SRI International, Menlo Park, CA, May 1996.
- [2] M. Hackett, K.-L. Ring, T. Schellenberg, M. Tashiro, *High-performance Thermoplastics, Speciality Polymers in Speciality Chemicals*, SRI International, Menlo Park, CA, 1996.
- [3] D.W. Van Krevelen, *Properties of Polymers*, Elsevier Science B.V., Amsterdam, 1990.
- [4] J.D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1980.
- [5] N.G. McCrum, B.E. Read, G. Williams, *Inelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, reprinted by Dover Publications, New York, 1991.
- [6] V.B.F. Mathot, *Calorimetry and Thermal Analysis of Polymers*, Hanser Gardner Publishers, Cincinnati, OH, USA, 1994.
- [7] R.P. Chartoff, in: E.A. Turi (Ed.), *Thermal Characterization of Polymeric Materials*, 2nd ed., Ch.3, Academic Press, San Diego, CA, 1997.
- [8] H. Suzuki, J. Grebowicz, B. Wunderlich, *Br. Polym. J.* 17 (1985) 1.
- [9] M. Alsleben, C. Schick, *Thermochim. Acta* 238 (1994) 203.
- [10] R.J. Seyler, *J. Therm. Anal.* 49 (1997) 491.
- [11] C. Schick, J. Dobbertin, M. Pötter, H. Dehne, A. Hensel, A. Wurm, A.M. Ghoneim, S. Weyer, *J. Therm. Anal.* 49 (1997) 499.
- [12] B. Wunderlich, *J. Therm. Anal.* 49 (1997) 513.
- [13] J.B. Miller, *J. Therm. Anal.* 49 (1997) 521.
- [14] S.X. Lu, P. Cebe, *J. Therm. Anal.* 49 (1997) 525.
- [15] B.B. Sauer, 11th ICTAC, Philadelphia, PA, USA, August 12–16, 1996, p. 381.
- [16] K.H. Gardner, J.S. Freida, in: *Proc. 46th Annual Conf. on Applications of X-ray Analysis*, Steamboat Springs, CO, USA, August 4–8, 1997.
- [17] M.Y. Keating, *Proc. 7th European Symp. on Thermal Analysis and Calorimetry*, Balatonfüred, Hungary, August 30–September 4, 1998.
- [18] M.-F. Cheung, A. Golovoy, H.K. Plummer, H. van Oene, *Polymer* 31 (1990) 2299.
- [19] V.L. Rao, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* C35(4) (1995) 661.
- [20] F.P. Glatz, R. Mülhaupt, *High Perform. Polym.* 5 (1993) 219.
- [21] M. Davies, J.N. Hay, B. Woodfine, *High Perform. Polym.* 5 (1993) 37.
- [22] J.D. Menczel, M. Jaffe, W.E. Bessey, in: E.A. Turi (Ed.), *Thermal Characterization of Polymeric Materials*, 2nd ed., Ch. 8, Academic Press, 1997, 2040 pp.