Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

THERMAL PROPERTIES OF POLYCARBONATE GRADE BISPHENOL A

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Abstract

Thermal properties of 4,4′(2,2′-propylidene)-diphenol, referred to as bisphenol A, or BPA, are discussed. Parameters of thermal transitions were measured by DSC. The commercial product crystallizes in α-form crystals which melt at 157°C (onset) and 161°C (peak) with a heat of fusion 134.37 J g^{-1}. Supercooled BPA shows a glass transition at about 40°C. Almost identical results were obtained for samples recovered by different methods: flakes, pastilles and prills. Two new polymorphs, the β and γ-forms were identified. The β-form melts at 131°C with a heat of fusion of 104.9 J g^{-1}. The melting point of the γ-form was measured to be 138°C and its heat of fusion is 118.3 J g^{-1}. Thermal conductivity of crystalline BPA was measured.

Keywords: bisphenol A, crystallization, glass transition, melting, polymorphism, thermal conductivity

Introduction

Bisphenol A (BPA) is widely used as a building block for the formation of a variety of polymers. In particular, the reaction with epichlorohydrin, producing the diglycidylether of bisphenol A, forms the basis of most epoxy resin manufacture. Commercial polycarbonate is also based on bisphenol A, for which very high purity material is required. Other useful polymers produced using BPA are phenoxy resin and polyethersulphones.

Crystallization is one of the oldest of the chemical engineering unit operations and a major product recovery process in the chemical industry [1]. Polycarbonate grade BPA produced by Shell Chemical Co. in the U.S. is currently recovered by the flaking method in which the melt flows over the surface of a cold drum where it crystallizes. Two alternate methods have been developed for industrial applications: pastillation and prilling. Pastilles are obtained by placing liquid droplets on a moving chilled stainless steel belt where they solidify in the form of semi-spherical particles. The prills in turn are solidified by dispersing BPA droplets in an inert gas and their shape is close to spherical.

Szap *et al.* [2], have analyzed the chemical purity of bisphenol-A using a high pressure liquid chromatograph (HPLC) method. Thermal properties, including heat capacity and thermodynamic functions of BPA and some of its reactive systems and blends, were addressed in several papers [3–5]. Dugacheva and Popurij studied zone melting of BPA [6]. Belskij *et al.* [7] analyzed crystal structure, molecular conformations and packing based on X-ray diffraction. He was able to identify up to three independent conformers that are distinguished by rotation of benzene rings.

The melting point typically observed for BPA is 157°C. As we learned during this study, alternate crystalline forms can also be obtained by changing crystallization conditions. Each polymorph has a different morphology and melting temperature. The scope of this work was to study thermal properties of BPA with the main focus on the parameters of melting and the mechanism and kinetics of crystallization. The effects of recovery method and material purity on crystal structure are addressed as well.

Experimental

The main material studied in this work is polycarbonate grade BPA, a commercial product manufactured in flake form by Shell. Its purity is better than 99.95% as determined by HPLC. In addition, BPA prills produced by Shell Netherlands Chemical (SNC) and by Aristech and pastilles manufactured by Blachownia (Poland) were evaluated. All materials were characterized without any further treatment.

Phase transition measurements were performed with a Perkin-Elmer DSC7 and TA Instruments DSC. Both the temperature and the heat of fusion were calibrated using NIST certified standards.

Crystallization of BPA was investigated from both the melt and the glassy state. It was noticed that sample size is a factor in supercooling the melt and controlling the final structure. Two groups of samples were studied: "large samples" weighing between 5–20 mg, the usual weight used in DSC experiments, and "small samples" weighing between 0.5–1.5 mg. Cooling rates applied varied between 0.5–100°C min^{-1}. Homogeneous nucleation, "seeding" and "self-seeding" experiments were performed. Optical microscopy was done with a Leitz Laborlux 12 PoL S microscope equipped with a 35 mm camera and coupled with a Mettler FP-80 hot stage.

Thermal conductivity was measured with a Thermal Conductivity Analyzer-TCA 100 by Holometrix, which utilizes a guarded heat flow method. The measurements were performed on solid samples, using the "molten cell". Pyrex glass was used as a calibration standard. According to the vendor's data, the usual accuracy of the molten cell is about 3%. To prepare samples, liquid BPA was poured into the (inner) containment ring of 1.75 inch diameter and allowed

to solidify. Next, both the sample and the ring were planed down to a flat, even surface. Two samples of 3.7 mm thickness were made. (During preliminary tests, it was determined that the thickness had to be below 5 mm in order to be within the instrument calibration range.)
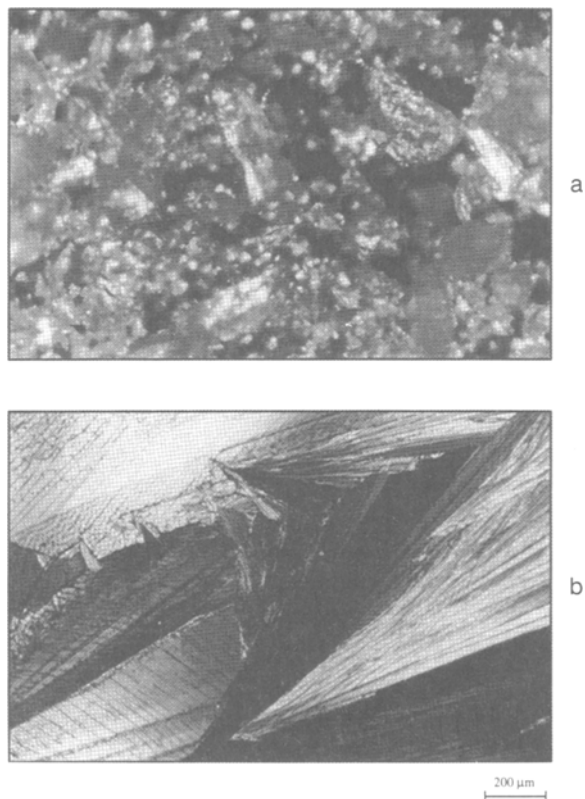
Fig. 1 Optical micrographs of Shell BPA: a) "as-received" flakes, b) crystallized from the melt on the glass slide

Thermal properties of the commercial product

Shell's commercial BPA is in the form of a white powder. Figure 1 shows the morphology of as-received material and the sample crystallized from the melt on a microscope slide. In Fig. 2a, DSC trace taken on Shell samples recovered by flaking is presented. The commercial product shows only one distinct endothermic transition which describes the melting process. No glass transition was recorded for "as-received" samples, indicating total crystallinity of the material. The parameters of melting measured at 10°C min^{-1} heating rate on Shell BPA were:

1. Onset of melting, T_{on} 157.0±0.8°C (430.2 K)
2. Peak temperature, T_p 161.5±0.8°C (434.6 K)
3. Heat of fusion, ΔH_f 134.37±1.99 J g^{-1} (30.794 kJ mol^{-1}).

The data represent the averages of 18 data points taken in two labs[*] and compare well with the data obtained by Novoselova *et al.* [3]. Identical thermal behavior was found for BPA produced by other vendors using different recovery methods, as shown in Curves b-d in Fig. 2.

In heat treated samples, several phenomena were observed depending on the effectiveness of cooling. On slow cooling (10°C min^{-1} or less), BPA usually crystallizes back to full crystallinity, showing the same melting characteristics as observed for as-received samples. Faster cooling of the melt shows both, a crystallization exotherm and the glass transition, indicating only partial crystallinity of the samples. On subsequent heating, the glass transition occurs in a relatively sharp step, between 37–42°C. It was noticed that with the heating and cooling rates applied in this work, the enthalpy relaxation during the glass tran-
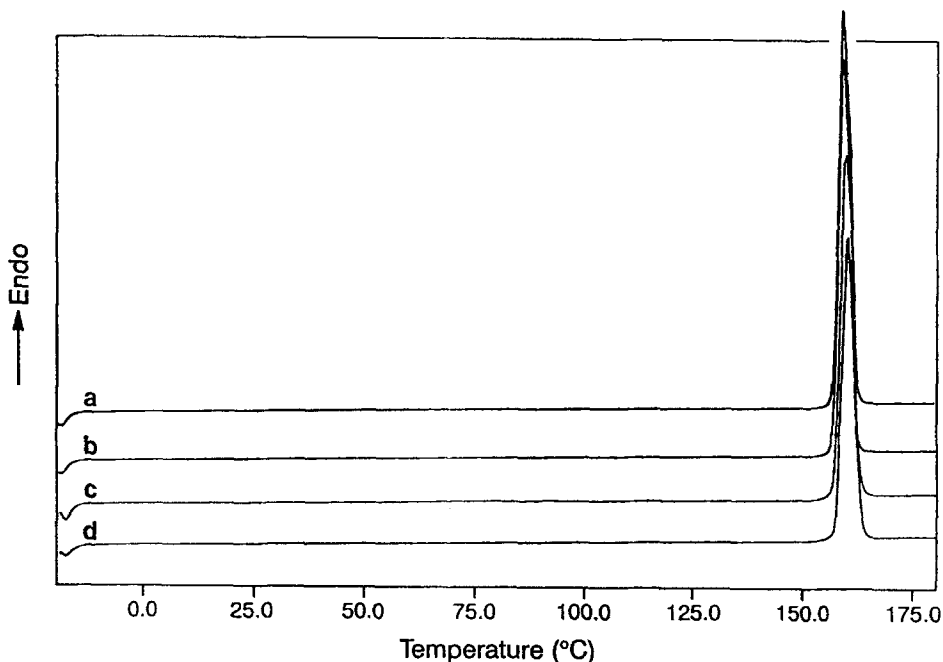

Fig. 2 DSC traces of commercial BPA recovered by different methods: a) Shell-flakes, b) SNC-prills, c) Aristech-prills and d) Blachownia-pastilles

sition was highly reduced (for the discussion of enthalpy relaxation in glasses see for example Refs [8–10]). Between 55–70°C, cold crystallization takes place. Melting usually occurs at 157°C. In most cases, single crystallization and melting peaks were observed, but multiple transitions were recorded as well. As will be described below, we were able to identify up to three different crystal forms in samples crystallized at different conditions. This was most easily observed in small samples subjected to fast cooling.

Thermal conductivity was measured on crystalline samples in the temperature range 30–140°C. In Table 1, the average values of two measurements are given.

The data show linear relationship with temperature and can be fit into:

$$k = 8.84 \cdot 10^{-1} \cdot T + 2.013$$

where: k is thermal conductivity in W mK^{-1}, and T-temperature in °C.

The calculated data show about a 5% increase in the temperature range of interest. Measurement of thermal conductivity of molten BPA was not attempted due to the inability of the instrument to handle low viscosity liquids.

The heat capacity of bisphenol A is currently being evaluated and will be the subject of a separate paper [12].

Polymorphism–morphology

Crystallization from the melt: α-form

When a thin film of molten BPA is cooled to room temperature in the absence of outside interference, it crystallizes easily forming large crystals as shown in Fig. 1b. The process is very fast and difficult to monitor. In order to get better insight into this transition a series of experiments was performed involving different temperatures and nucleation mechanisms.

Table 1 Thermal conductivity of bisphenol A

Temperature/ °C	Thermal conduct./ W mK^{-1}
30	2.01
50	2.07
70	2.11
90	2.09
110	2.09
130	2.12
140	2.14

First, samples were melted on the glass slide, cooled to a selected temperature (150, 145 or 70°C), and then tiny powder particles of BPA (seeds) were added on the surface. At 150 and 145°C, crystallization occurred instantly and crystal development could not be recorded with the camera. To slow the crystallization rate, the molten sample was first supercooled to the glassy (isotropic) state by immersion in liquid nitrogen and later its temperature was raised to 70°C. This temperature is close to the temperature of cold crystallization, but during this step the sample stayed amorphous for a few seconds because of the lack of nuclei. At the moment the nuclei were added from the outside, the growth of crystals started. However, due to the high viscosity of the material at this temperature, the process was slow enough to allow controlled microscopic observation. In Figs 3a–c, development of spherulitic crystals around solid nuclei is pictured.

After the crystallization process was completed, each sample was analyzed by DSC which showed the melting endotherms at 157°C and revealed 100% crystallinity of the material.

In the commercial flaking process, the molten BPA flows over the layer of solid and, therefore, it has some brief contact with crystals. To better understand the effect of such interaction on the crystallization process and the structure of the final product, a partial melting experiment was performed. Virgin samples were heated inside the DSC cell and their melting monitored by visual observation of the DSC trace on the screen. After the melting peak reached approximately 1/3, 3/4, and full height, each sample was cooled to –40°C at 100°C min^{-1}. Such a procedure allowed some crystals to be left intact so that during the cooling cycle samples crystallized with the remaining crystals acting as self-seeded nuclei. (This seeding phenomenon is the subject of the paper by Blundel and Keller [11].) When the samples were analyzed on heating, smooth DSC traces were recorded in all cases showing the melting process at 157°C and crystallinities close to 100%.

Since the melting of crystals grown by any of the above method occurs at 157°C as the only transition, we conclude that these crystals represent the same crystal form with spherulites being their characteristic morphology. We call this polymorph the α-form.

## Crystallization from the glass: β-form

While experimenting with small samples it was noticed that it is not only easy to supercool the melt to the glassy state, but also different types of crystals can be grown from the glass.

For DSC experiments, small BPA samples were first heated to 200°C (well above the melting point), and then cooled to –50°C at rates between 1–300°C min^{-1}. Next, each sample was reheated at 20°C min^{-1} for analysis of

phase transitions. In Fig. 4, DSC traces taken on 0.79 mg samples cooled at different rates are compared with the data obtained for as-received material. Fresh samples show only one endotherm at 157°C (Curve a). For samples cooled at the rate of 20°C min^{-1} and higher, DSC indicates a complex phase structure (Curves b and c). Besides the glass transition and one or more cold crystallization peaks, a new, strong melting peak is observed. The peak has its onset at 131 and its maximum at 136°C. It can vary in magnitude and can exist as a companion to the "normal"(α-form) endotherm (Curve b) or become the only melting peak (Curve c).

100 µm
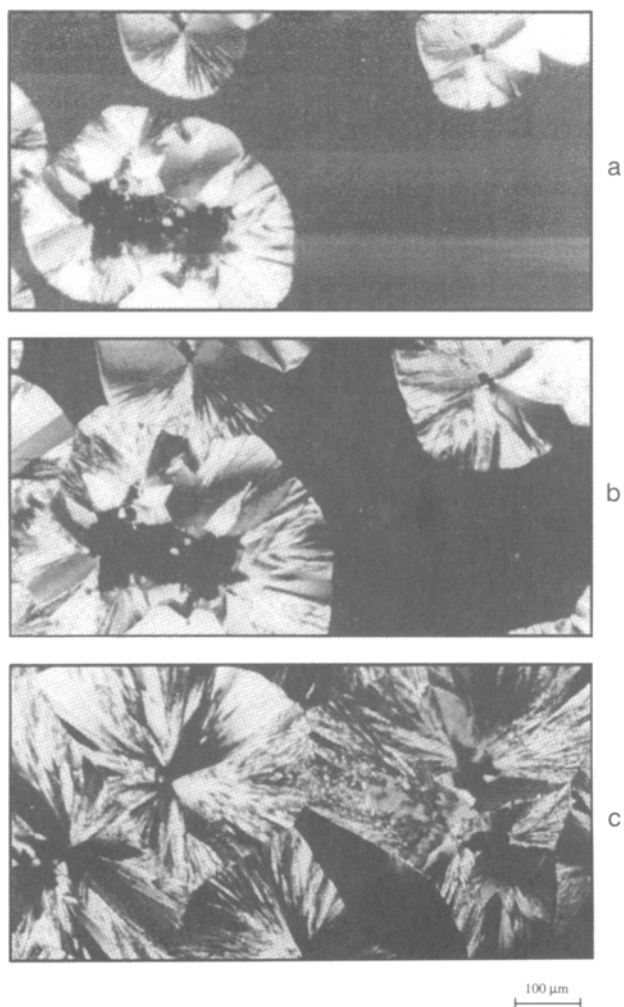
Fig. 3 Development of spherulites around "seeds" during crystallization of BPA at 70°C
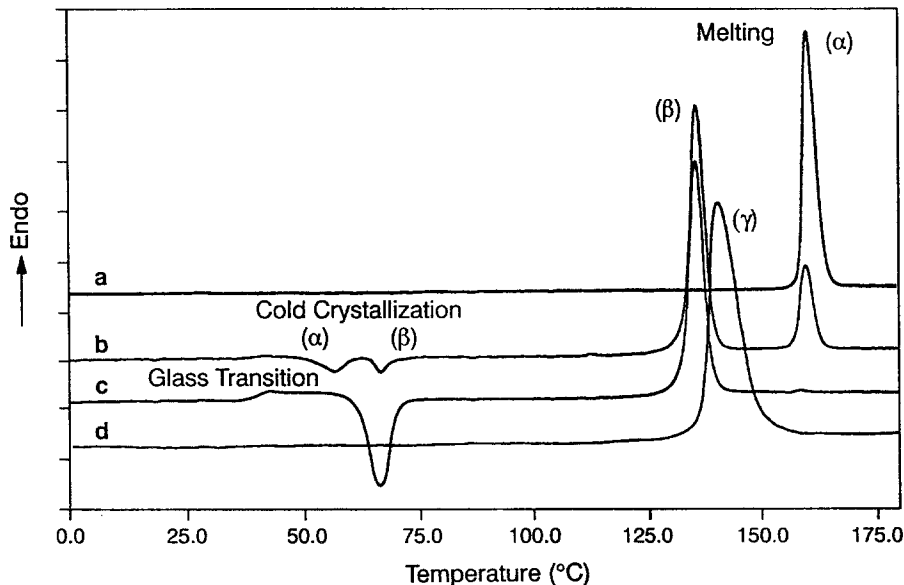
Fig. 4 DSC trace of Shell BPA taken on heating at 20°C min^{-1}. Sample history: a) as-received, b) cooled at 20°C min^{-1}, c) cooled at 50°C min^{-1}. Sample weight 0.79 mg. Curve d): sample weight 0.165 mg, cooling rate 300°C min^{-1}, heating rate 50°C min^{-1}

It was speculated that this peak represents melting of a different crystalline form. In order to verify this assumption, optical microscopy was used. Samples were prepared in steps. Firstly, small particles of BPA were melted on the microscope glass slide and cooled by immersion in liquid nitrogen. Next, the samples were allowed to crystallize at room temperature for several hours and their structure checked periodically.

Figures 5a–d show photographs of the crystallization process. Freshly cooled samples are isotropic, as revealed by optical microscopy with crossed polarizers. Typically, after a few minutes needle-like crystals appear, but droplets of totally amorphous BPA were observed up to 1 hour after vitrification. Within each droplet, the crystals are distributed randomly with respect to their position and orientation. Usually a larger number of crystals of different length are observed. The size distribution clearly indicates that the nucleation is not instantaneous. In one instance, a 215 μm long crystal was formed – the largest single needle observed in this work. At some point in time, crystals of different type develop in the form of spherulites (Figs 5b–d). Their nucleation was spotted either in the bulk, on the edge of the droplet, amongst the dense population of needles or in isotropic areas. They grow much faster than the needles and consume all isotropic material available, including needles which were previously developed. Observation of both types of structures may sometimes be difficult due to a large difference in brightness.
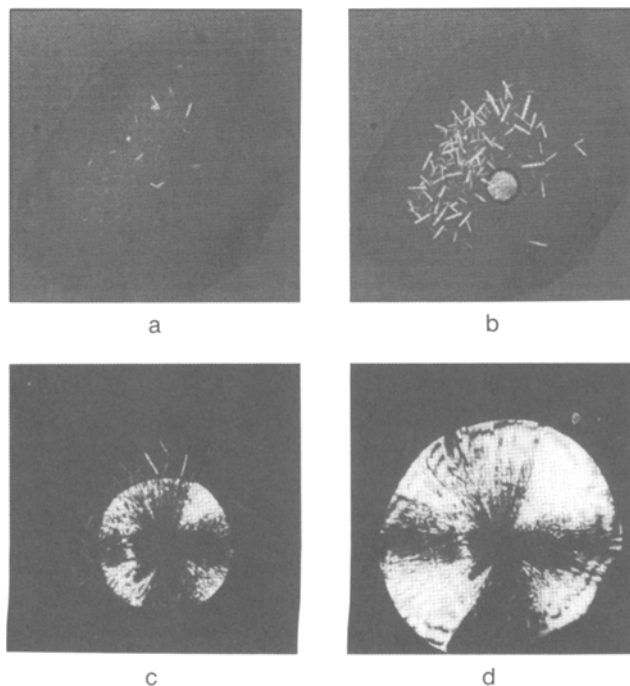
Fig. 5 Crystallization of BPA from the glass at 25°C. Time elapsed after cooling in liquid nitrogen: a) 1115, b) 1710, c) 1718 and d) 1727 sec

The effect of temperature was studied using hot-stage optical microscopy. When two or more droplets of different crystal morphology were identified in the viewing area, the specimen was heated at 10°C min^{-1} and changes of the two structures were directly compared as a function of temperature. The results are given in Figs 6a–f. Figure 6a, shows three droplets crystallized with spherulitic morphology (characteristic of α-form) and two with the needle-like structure. As the temperature increases, cold crystallization is observed above 45°C. This effect is best seen in "β-droplets" since their partial crystallinity at room temperature was most visible (Fig. 6b). At 131°C, melting of needles occurs while spherulitic crystals are left intact (Figs 6c, d). They melt at 157°C – the melting point of the α-form. Based on both crystal morphology and melting temperature, we conclude that needles represent a different polymorph which we now call the β-form.

Hot-stage microscopy provided a good illustration of all thermal effects recorded by DSC as shown in Fig. 4 (Curves b and c) and, therefore, allowing classification of the 157°C peak as melting of the α-form, and the 131°C peak as melting of the β-form.
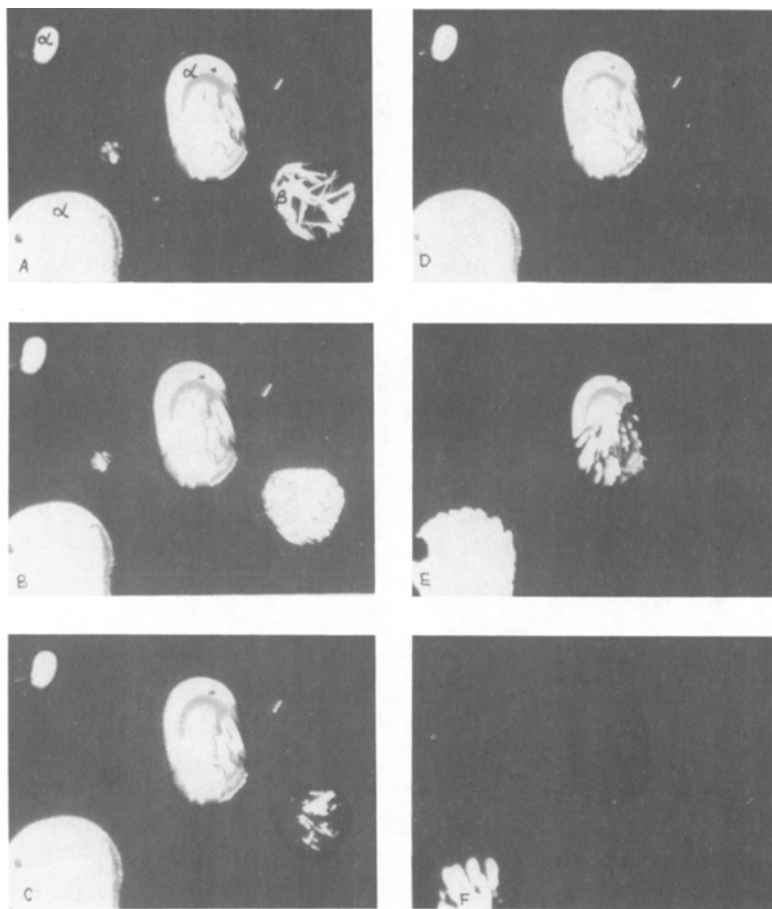
Fig. 6 Optical micrographs of α- and β-form crystals at different temperatures: A) 30, B) 70, C) 133, D) 146 and E-F) 157°C

Kinetics

For crystallization kinetics studies the sample was melted on the microscope glass at 160°C and spread to form a thin film (which usually broke into droplets and streaks). Next, the sample was quenched by immersion in liquid nitrogen to solidify. The structure was observed under the optical microscope at room temperature (25°C). Photographs of growing crystals were taken at controlled periods of time (similar to that shown in Fig. 6) and used for kinetic measurements.

The growth rate of needle-like crystals was measured as an increase of their length with time. The average value obtained from 13 data points is 0.04 $\mu m\ s^{-1}$. It was assumed that the growth rate is a linear function of time.

The growth rate of spherulites was measured as the speed of their boundaries moving along the radius. The average of 11 data points taken on five spherulites is 14.5 $\mu m\ s^{-1}$, which means that spherulites (characteristic for the α-form) grow about 360 times faster than needles (characteristic for the β-form) crystals.

In thicker samples a larger population of spherulites develops. At any given time, both morphologies show considerable size distribution, which is an indication that neither nucleation process is instantaneous.

Spherulites are much less numerous than needles. Their formation seems to be an independent process. In the glassy state, nucleation rate and nucleation density of needles are higher than those observed for spherulites. However, due to the much higher growth rate, spherulites eventually override needles and terminate their growth.

The effect of purity: γ-form

As stated previously, samples of virgin BPA produced by different vendors show identical melting behavior. This is, however, not the case in heat treated materials. In Fig. 7, DSC traces of samples cooled from the melt at 200°C min^{-1} are shown and corresponding numerical data obtained from these analyses are given in Table 2.

DSC indicates that none of the samples reached full crystallinity during cooling. The SNC material became about 92% crystalline and has the highest crystallinity of the three. The remaining 8% crystallizes at about 70°C during the heating cycle. Its crystals melt at 157°C indicating that all crystallinity observed in the SNC sample constitutes the α-form. The Aristech sample became of much lower crystallinity upon cooling. DSC shows a large step at the glass transition temperature 39°C. At 62°C, a substantial cold crystallization peak is recorded and at 132°C melting. The melting point is a clear indication that the crystals are in the β-form. The heat of fusion was measured to be 104.1 J g^{-1}.

The Blachownia sample behaves very different. It not only shows two cold crystallization peaks (at 67 and 104°C, onset temperatures) but also a new melting peak at 138°C, considerably higher than that for the melting of the β-form.

Since it was suspected that purity may play a role in the formation of different crystal forms, two other experimental grade samples were studied. Their purity was A-99.85 and B-95%. Both as-received samples crystallized in α-form. Sample A melts at 157°C and is 100% crystalline. Sample B has a broader melting peak with an onset temperature of 154°C. Its heat of fusion accounts for only 89% crystallinity. On cooling from the melt, each sample shows

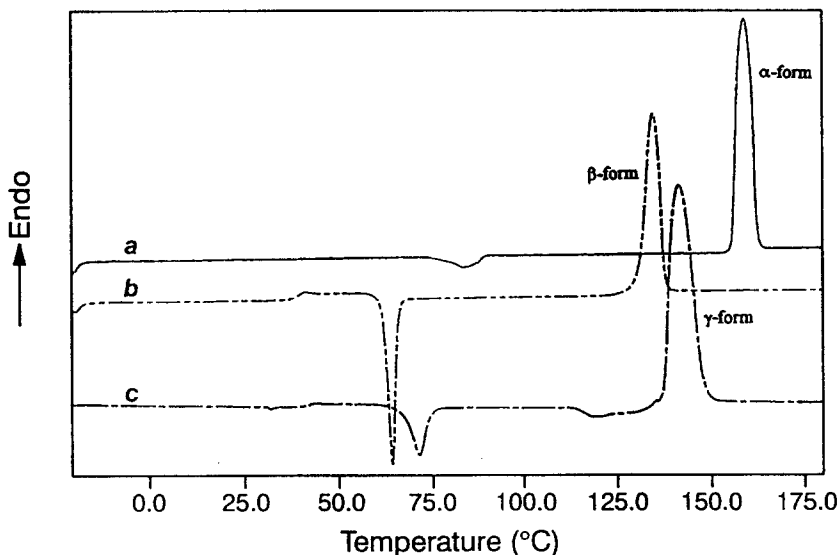**Fig. 7** DSC heating traces of BPA crystallized by rapid cooling at 200°C min^{-1}. Sample designation: a) SNC, b) Aristech and c) Blachownia

Table 2 Parameters of thermal transitions in BPA rapidly cooled from the melt

Sample	T_g / °C	T_{cc} / °C	ΔH_{cc} / J g^{-1}	T_m / °C	ΔH_f / J g^{-1}	Weight/ mg
SNC[a]		74	11.8	157	134.2	6.29
Aristech[b]	39	62	55.3	132	104.1	6.12
Blachownia[c]	41	67	17.9	138	118.3	4.99
		114	10.6			
Shell[d] (Fig. 4d)	–	–	–	138	118.4	0.79

[a] Shell Nederland, The Netherlands
[b] Aristech Chemical Co., USA
[c] Zaklady Chemiczne Blachownia, Poland
[d] Shell Chemical Co., USA

both crystallization and glass transitions (Fig. 8). Sample B has a smaller crystallization peak and much more pronounced glass transition, indicative of lower crystallinity. Consequently, it has also a much bigger cold crystallization peak on the next heating. Both samples have two melting peaks. The main peak in sample A is 157°C (α-form) while sample B shows it at 131°C (β-form). Beside the main peak, each sample has a smaller endotherm at 138°C, the temperature identical to that measured on Blachownia sample (Fig. 7c). Interestingly enough, a similar peak was recorded also on Shell BPA (high purity) when a

very small sample (0.79 mg) was cooled at 300°C min^{-1} and reheated at 50°C min^{-1} (Fig. 4, Curve d).

Since in both Shell and Blachownia cases the endotherm at 138°C is the only melting process observed in the whole temperature range, one can assume that the peak represents melting of yet another crystal form. We propose to call it the γ-form. The recorded heat of fusion for this form is 118.3 J g^{-1}. These observations suggest that both fast cooling and the presence of impurities may influence the formation of different polymorphs.

Orientation Induced Crystallization

Scratching the surface of the amorphous (glassy) or partially crystalline BPA with a sharp pin causes immediate crystallization with spherulitic morphology. The orientation of the molecules by the pin's tip motion induces nucleation and growth of crystals in the direction from the scratch. In Fig. 9, development of spherulites along the scratch line is depicted. Prior to scratching, the sample shown in Fig. 7 was already crystallized for about one hour with needle-like β-form. Scratching induces crystallization of α-form which is much faster than that of the β-form and the completion of the crystallization process took only a few seconds.

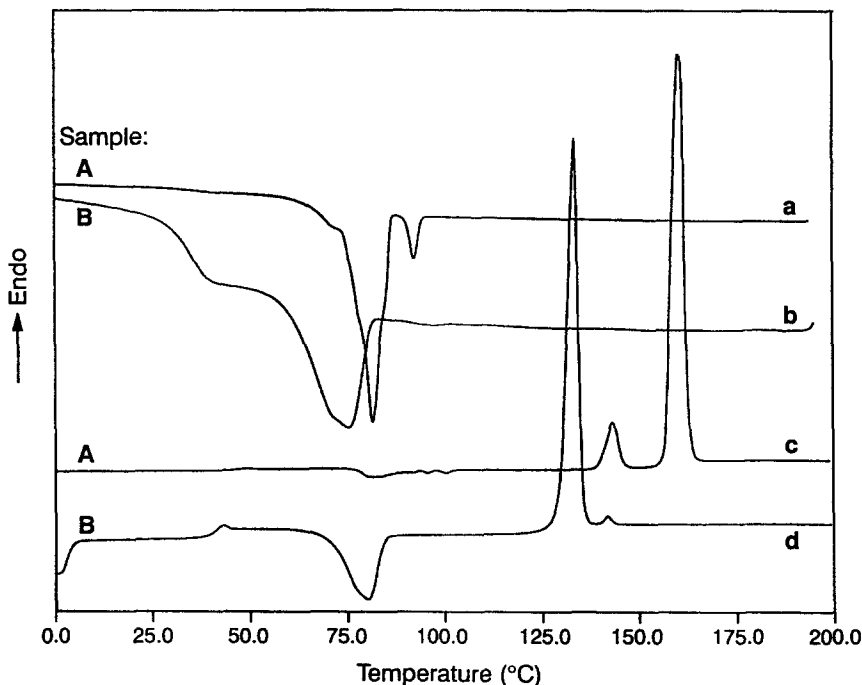**Fig. 8** DSC traces of lower purity BPA taken on: cooling (a, b) and heating (c, d) at 20°C min^{-1}. Sample purity: A-99.85% and B-95%. Sample weight 6 and 10 mg
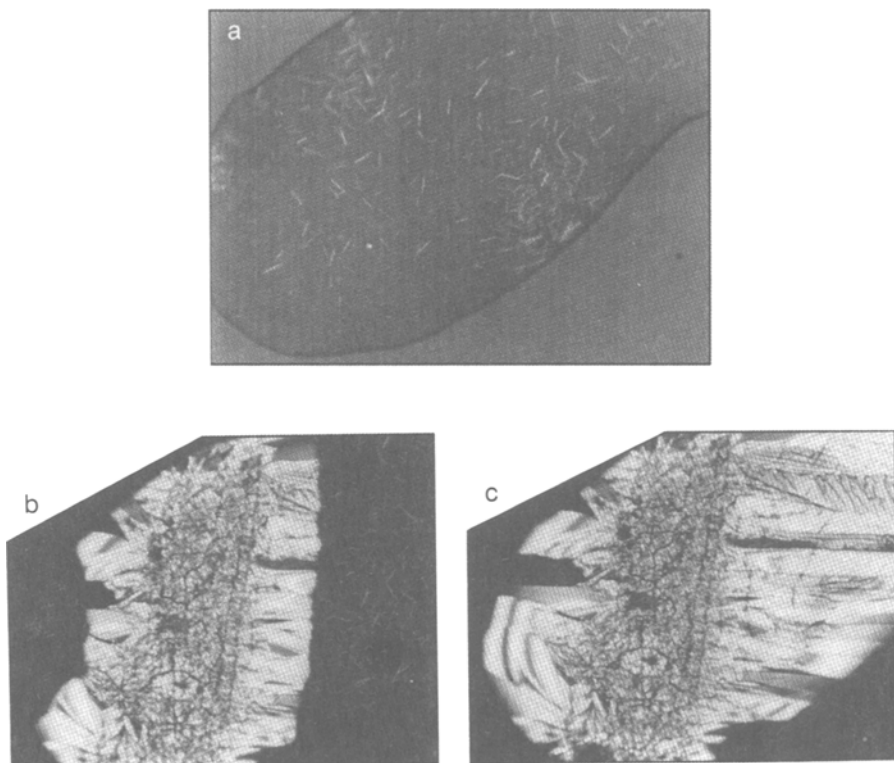
Fig. 9 Development of spherulites along the scratch line in Shell BPA

Discussion

Commercial BPA is a crystalline material having the same crystal structure (α-form) regardless of the recovery method applied in the production process. The experiments showed that fast cooling of the molten BPA can result in a totally glassy state. BPA is capable of crystallizing below T_g, but the crystallization rate drops several orders of magnitude compared with the rate observed above T_g. Supercooled bisphenol A can crystallize in three different processes, each having an independent nucleation, different kinetics and resulting in crystals of different morphology and melting temperature. This is an indication of different polymorphs of BPA formed depending on the thermal history of the sample. Figure 10 summarizes temperatures of phase transitions as a function of cooling rates. The diagram indicates that the formation of the β-form requires cooling of the melt at 20°C min^{-1} or faster. Cold crystallization of both α- and β-forms occurs at similar temperatures (average), but the temperature range for

the formation of α-form is wider (about 12 degrees) than that for β-form (about 2 degrees). The closeness of the two regions may complicate proper interpretation of DSC traces. The formation of the γ-form requires much faster cooling. This process may be induced by impurities present in the material. The schematic in Fig. 10 may serve as a guide to the conditions necessary to create different physical states of BPA. Different stability ranges for each polymorph are clear indications of different packing in crystal unit cell and intermolecular interactions. Further research is needed to relate the thermal transitions of BPA
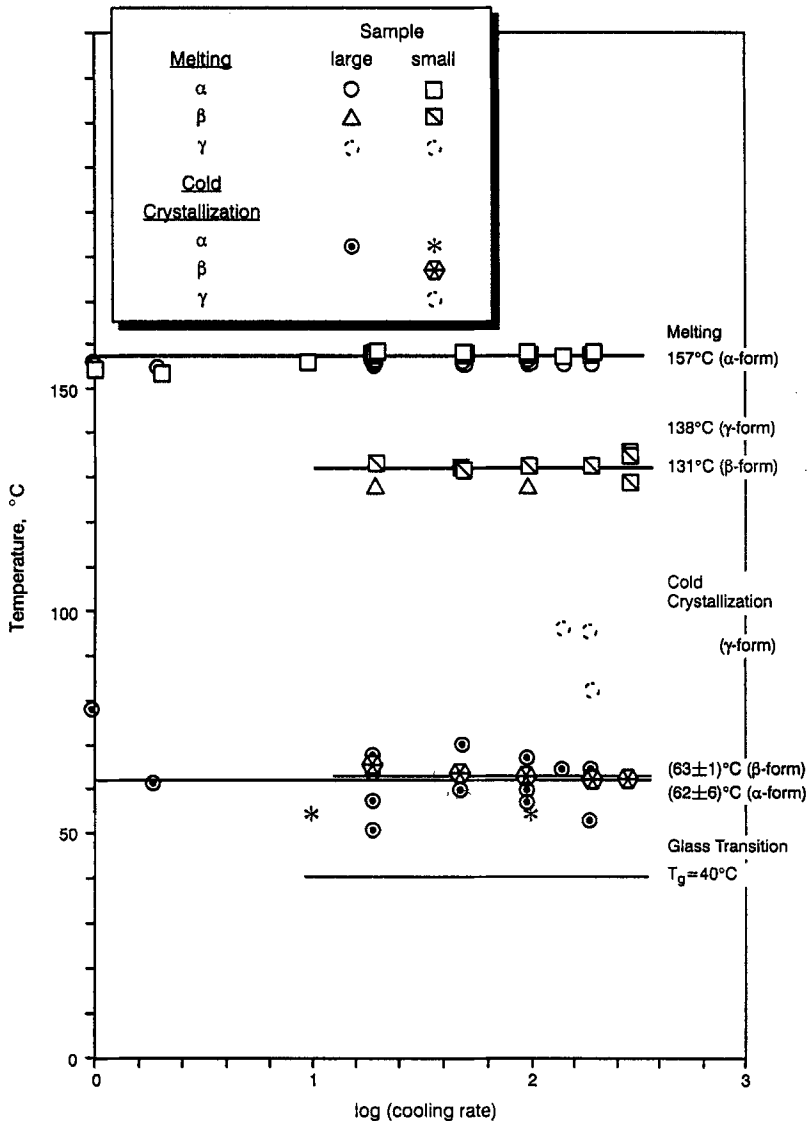

Fig. 10 Temperatures of phase transitions in BPA as a function of cooling rate

with structural details of each crystal form and molecular conformation in particular. Equilibrium melting data for both β-and γ-forms should be verified as well.

Conclusions

Based on the current work, BPA can exist in five physical states: liquid, glass and three crystal modifications: α, β and γ. The growth of the β-form is two orders of magnitude faster than the α-form. Nucleation by "seeding" causes rather fast growth of the crystal (instantaneous at higher temperatures) and results in almost total crystallinity. This is the most likely mechanism taking place during industrial recovery. Fast cooling from the isotropic melt in the absence of nuclei results in a glassy state or partial crystallinity. Mechanical deformation (scratching) and/or annealing of partially crystalline samples above the glass transition increases crystallinity up to 100%, as observed in the commercial product.

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