Multiple transitions in poly(allylbenzene): 1. Thermophysical properties

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Polyallylbenzene is a semicrystalline material the thermal behaviour and physical properties of which reveal several transitions. Thermal and differential calorimetric analysis have shown the influence of the history of the material about the glass transition and melting. Several techniques such as thermomechanical analysis, dilatometry and inverse gas chromatography give additional information for the unidimensional and volume behaviour of the polymer *versus* temperature.

(Keywords: poly(α-olefin); poly(allylbenzene); thermal properties; volume transitions)

INTRODUCTION

Different syntheses of poly(allylbenzene) have been carried out and the analysis of the molecular and structural characteristics have provided much information about it[1].

In this paper, we will consider thermophysical properties of this polymer and in an accompanying paper, the electrical properties of this material will be presented.

The observed correlations between the structure of the polymer and its various properties allowed the construction of a morphological model. In the work presented here, the thermal and volume transitions of the polymer, which can be assigned to amorphous and crystalline regions will be specified.

EXPERIMENTAL

Materials

Poly(allylbenzene) (PAB)[1] was synthesized by Ziegler–Natta polymerization with a VCl_3-$Al(C_4H_9)_3$ catalyst–cocatalyst system at a temperature of 50°C for 72 h. The number-average molecular weight $\bar{M}_n$ as determined by gel permeation chromatography (g.p.c.) at 135°C in *o*-dichlorobenzene was 180000 with $\bar{M}_n/M_w = 4.5$ and $\bar{M}_z/\bar{M}_w = 3.7$. The polymer density measured with a Davenport gradient column at 20°C in a methanol–1,2-dibromoethane mixture was 1.078. The polymer was used either as powder A_p or film A_f according to the technique used. The films were moulded in vacuum under $590 \times 10^4\,N\,m^{-2}$ pressure at a temperature $T_m = 204°C$. Cooling rates were $20°C\,min^{-1}$ for film A_{f_1}, $0.4°C\,min^{-1}$ for film A_{f_2} and a third film A'_f was quenched in liquid nitrogen.

Analysis techniques

*Differential thermal analysis.** Thermal behaviour of the polymer powder or films was studied with a DuPont 990 Thermal Analyser, with 6 to 10 mg samples.

The heating rate was $600°C\,h^{-1}$ in the range −150°C to 300°C.

*Differential scanning calorimetry.** Measurements were made with a DSC Mettler TA 2000 B, flushed with argon. Details of the techniques and values of the temperature and the enthalpy of melting of standards used for the calibration of the system were published previously[2]. Enthalpies were considered to have a probable error of about 5%. The temperature was obtained with a precision of ±0.2°C. The sample mass was in the range of 6 to 10 mg. Heating and cooling rates of $300°C\,h^{-1}$ were used.

Thermal degradation. The study of sample degradation was carried out with a Mettler HE 20 apparatus, which allowed simultaneous recording of the temperature rise and the weight loss of polymer.

Thermal mechanical analysis. A DuPont 942 thermomechanical analyser was used as a plug-in module with the 990 Thermal Analyser. A flat-tipped expansion probe was held in gentle contact with the surface of the pellets A_p or film A_f placed as the bottom of a quartz cell fitted on a support. The samples were 200 μm thick on $1.13\,cm^2$.

The probe transmitted all thermal effects yielding a vertical displacement, i.e. linear expansion or shrinkage of the polymer to the core, which generated the electrical signal to the recorder. The probe supported a 2 g weight to increase the transitions.

The experiments were carried out in the range of temperature −25 to 170°C at heating rate of $300°C\,h^{-1}$.

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*These two techniques reveal two types of transition in polymers:

- the glass transition, which is considered as a second-order transition with a change of heat capacity C_p, but normally with no latent heat of transition. Consequently dC_p/dT was recorded and the glass transition temperature was taken as the first breakpoint of the thermogram baseline
- the first-order melting transition, occurring at constant temperature, with a change of enthalpy. The melting point temperatures were taken as the maximum of the corresponding peaks

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Dilatometry. Volume expansion or shrinkage measurements versus temperature were carried out on a 168 mg sample of film, placed in a glass dilatometer with a 2 mm diameter capillary. The dilatometer was filled with 73.2 g mercury. The variations of the mercury level resulting from the expansions of the polymer were detected by displacement of an electrical spot[3]. The heating rate was 1°C min^{-1} in the range of temperature 20°C to 230°C.

Inverse gas chromatography. One application of this technique[4] studies the diffusion of volatile liquids in the polymer used as a stationary phase. The retention diagrams clearly show the relaxations due to molecular motions.

An I.G.C. 16 Intersmat chromatograph with a thermal conductivity detector was used. The measurements were carried out in the temperature range 30°C to 170°C with helium as a carrier gas at a volume flow rate of $50\,\mathrm{cm}^3\,\mathrm{min}^{-1}$. Benzene was injected into the steel column, 24 cm long and 0.635 cm in diameter, filled with 1.263 g of poly(allylbenzene). The specific retention volume V_g of benzene vapour in the chromatographic column was determined, corresponding to the mass unity of the stationary phase and converted to 273 K. The measurements were carried out every 5°C from $T=20$°C up to $T=90$°C, then by steps of 10°C up to $T=170$°C.

RESULTS

Thermophysical effects were not observed at low temperatures (−150°C, +20°C), except for the loss of water from the polymer, which was absorbed during the cooling of the samples. Therefore, we have restricted the studies to the two following temperature ranges: $20°\mathrm{C}<T<140°\mathrm{C}$ and $140°\mathrm{C}<T<230°\mathrm{C}$, in which two thermal transitions were reported in the literature[5].

Differential thermal analysis

(a) The DTA spectra of the powder (A_p) and of the film (A_{f_1}) are identical (*Figure 1*), the glass transition appears at $T_g=59$°C and the melting point at $T_m=204$°C:

- the thermal spectra of the film A_{f_2} present a glass transition at $T_g=52$°C and a better defined melting peak at $T_f=209$°C
- the thermal diagram A'_f shows two melting peaks at $T_m=199$°C and $T'_m=207$°C. Then this film was quickly cooled at $20°\mathrm{C\,min}^{-1}$ and heated again giving the recording A'_{f_1}. The T_g was shifted to a higher temperature and the melting peak was again broad and single like those of A_p or A_{f_1}.

(b) The d.t.a. spectrum in the melting zone for A_{f_1} is shown in *Figure 2* with different conditions of recording. It appears that the beginning of the thermal transition is about $T=126$°C and this wide shoulder at the melting peak must be identified. The enthalpy of fusion is about $540\,\mathrm{cal\,mol}^{-1}$.

Differential scanning calorimetry

D.s.c. measurements have confirmed the previous results and allowed, with a better sensitivity, the analysis of A_p according to the effect of annealing as well as the determination of enthalpy of the transitions.

(a) Diagrams of thermal behaviour of the polymer A_p in *Figure 3* are shown for two cycles of temperatures with heating and cooling rates of $10°\mathrm{C\,min}^{-1}$ and $20°\mathrm{C\,min}^{-1}$ respectively.

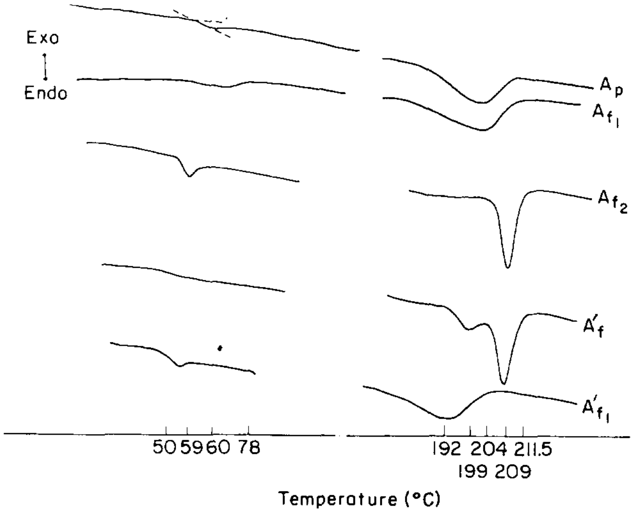

Figure 1 Thermal diagrams (d.t.a.) of poly(allylbenzene). A_p: powder; A_{f_1}: film cooled at $20°\mathrm{C\,min}^{-1}$; A_{f_2}: film cooled at $0.4°\mathrm{C\,min}^{-1}$; A'_f, A'_{f_1}: film heated at 204°C and quenched (A'_f: first heating; A'_{f_1}: second heating)

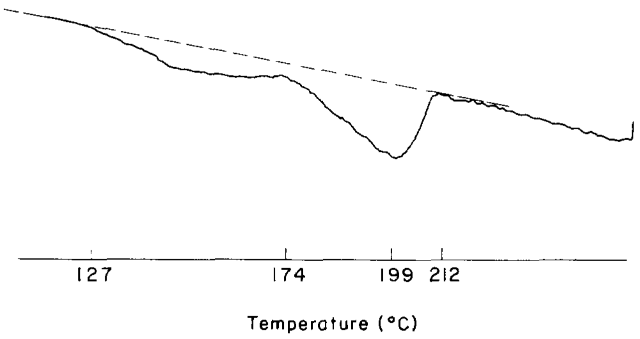

Figure 2 Thermal diagram (d.s.c.) of poly(allylbenzene) A_{f_1}

Cycle 1:—heating from 20 to 140°C
—cooling
second heating

Cycle 2—heating from 20 to 250°C
—cooling
second heating

During the first heating of cycle 1 and 2, the baseline unexpectedly increases towards the exothermic direction after T_g. This effect disappears completely only in the second heating of cycle 2 when the sample has relaxed all its internal stresses during the melting. Nevertheless the glass transition occurs at the same temperature in the different cases and is not modified by the melting of the polymer.

D.s.c. thermal spectra are better defined than d.t.a. spectra and two melting peaks can be seen in each case.

(b) The variations of the enthalpy at the passage of the transitions are shown in *Table 1*. ΔH_m is the variation of amount of heat corresponding to global melting peaks and ΔH_2 is the variation of enthalpy associated with the most important one.

Thermal effect of the glass transition ΔH_g is about ten times smaller than ΔH_m. Since the glass transition is an athermic phenomenon we confirm that this effect is an artefact.

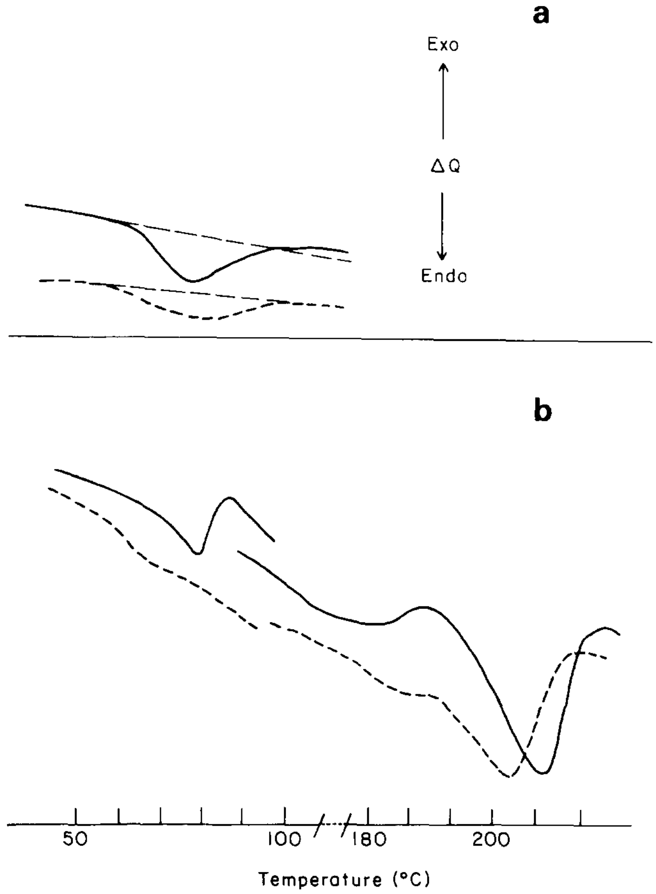

Figure 3 Differential calorimetric analysis of poly(allylbenzene) A_p according to two thermal cycles. Continuous curves correspond to the first heating, broken curves to the second heating of the sample. (a) cycle 1; (b) cycle 2

Thermal degradation

Figure 4 shows thermal degradation of 36.8 mg of A_p. The polymer exhibits high thermal stability up to 380°C (weight loss about 5%).

Thermal mechanical analysis

The experiments were carried out on the samples according to the thermal cycle 2 previously described over the range of temperature -25°C to $+170$°C. The variation of thickness *versus* temperature was plotted in *Figure 5* and dilatation coefficients λ were calculated for different ranges of temperature (*Table 2*).

In the interval $T = -10$ to 120°C, the recorded dilatation corresponds to $\lambda = 4.8 \times 10^{-4}$ c^{-1}. The abrupt variation of the polymer behaviour occurs at about T_g.

The polymers show nearly the same dilatation behaviour in the first or second heating. A certain flattening of the curves was observed between $T = 100$–140°C. It may be related either to the competition between the

Table 1 Enthalpy variations at transitions during cycle 2 in the indicated temperature range (I)

Polymer	Heating number	ΔH_g (J mol^{-1})	ΔH_2 (J mol^{-1})	ΔH_m (J mole^{-1})
A_p	1	-21.9 $I = 50$–100°C	92.6 $I = 184$–230°C	
	2	0		143.3 $I = 130$–223°C

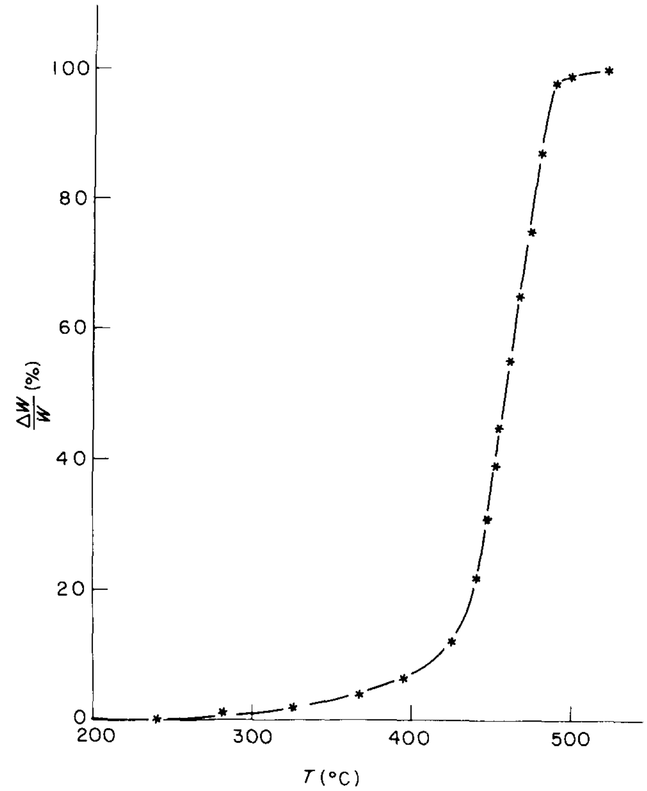

Figure 4 Loss of weight of poly(allylbenzene) recorded during degradation

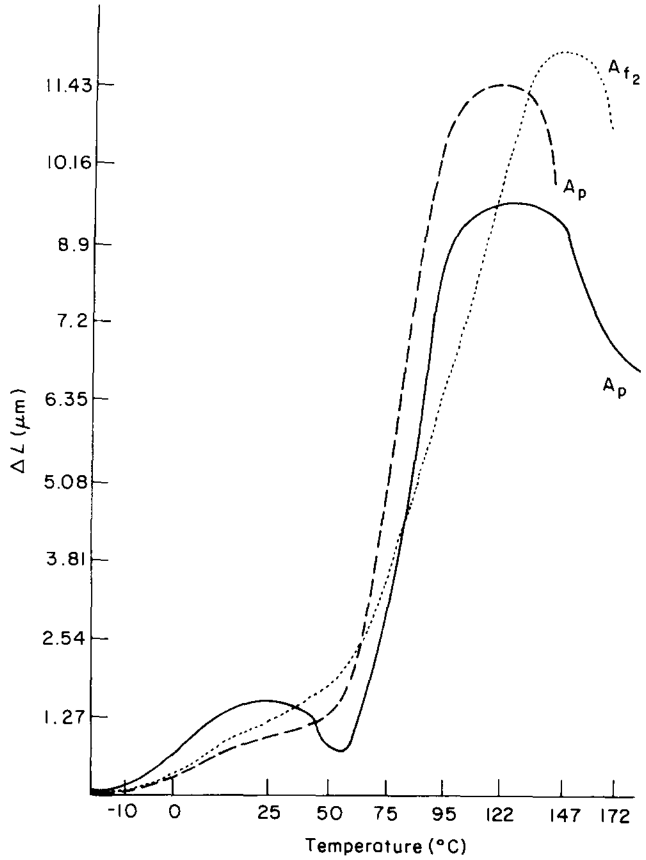

Figure 5 Recording of the variations of thickness for poly(allylbenzene) pellets A_p; (– – –): first heating; (———): second heating; and for poly(allylbenzene) film A_p (· · · ·)

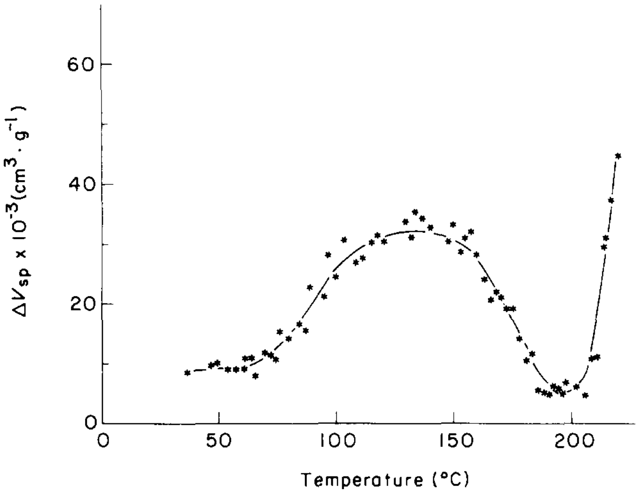

Figure 6 Variation of the dilatometric specific volume of poly(allylbenzene) *versus* temperature

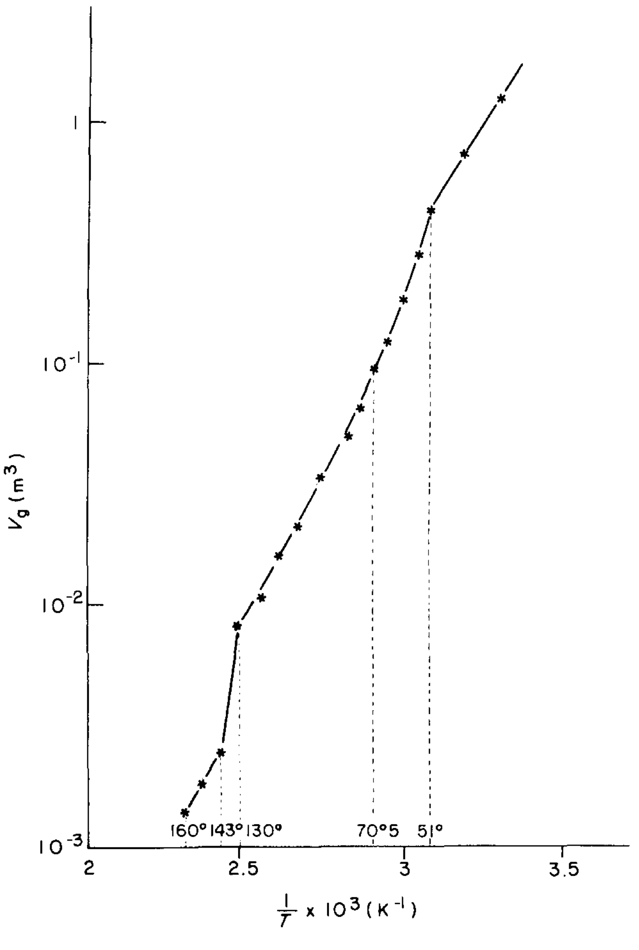

Figure 7 Specific volume vs. temperature^{-1}

Table 2 Linear dilatation λ and dilatometric α coefficients of poly(allylbenzene)

T (°C)	$0<T<60$	$60<T<100$	$150<T<200$	$200<T<230$
λ(°C)$^{-1}$	7×10^{-5}	3×10^{-4}	–	–
α(°C)$^{-1}$	2.5×10^{-4}	5×10^{-4}	-9×10^{-4}	28.4×10^{-4}

dilatation of the material and the penetration of the probe into the softening polymer or possibly a modification of the morphology.

Dilatometry

The change of the specific volume of the sample versus temperatures is plotted in *Figure 6*. A first variation was observed around the glass transition temperature and a regular increase was noticed up to about $T = 130$°C. Then, at higher temperatures, the specific volume decreased and above $T = 200$°C, a strong increase was again recorded, which can be related to the melting.

This result was confirmed three times under different experimental conditions, particularly with different quantities of the polymer. The dilatation coefficients α are given in *Table 2*.

Inverse gas chromatography

The plot of the retention diagram log $V_g = f(1/T)$ in *Figure 7* shows several changes of slope at 51, 70.5, 130 and 163°C.

DISCUSSION

All the phenomena investigated by different techniques give information related to glass transition, melting point and other transitions of poly(allylbenzene).

Repeated heatings of the samples illustrate the effect of annealing of the polymers and avoid interpretation of the transition after T_g as an intrinsic transition of the polymer. This exothermic effect after T_g is due only to the relaxation of the stresses stored in the polymer during sample preparation.

We have also verified with these different thermal scans that the unidentified transitions between 130 and 150°C are quite stable. The glass transition determined by the five techniques appears around $T_g = 51$–59°C, depending on the history of the polymer. This effect was observed[6] when the polymer was frozen after melting or annealed for some time at a temperature below or above the glass transition temperature. Such behaviour has already been described for polystyrene[7,8]. Inverse gas chromatography indicates a transition at 71°C which is assigned to a second glass transition studied in the following paper[13].

As poly(allylbenzene) is a semicrystalline polymer, T_g depends also on the crystallite types in the polymer: T_g of A_p is 59°C and T_g of A_{f_2} is 52°C. The melting peaks are narrow or broad according to the number and the size of the crystallites[9]. During very slow cooling (0.5°C min^{-1}) the crystallites of film A_{f_2} have larger and more regular dimensions than those of the rapidly cooled film A_{f_1} (20°C min^{-1}). The narrow melting peak corresponds to this more perfect structural organization and $T_m = 209$°C is higher for film A_{f_2} than for A_{f_1} ($T_m = 204$°C).

The chain motions in the amorphous range are also influenced by the nature of the crystalline domains as seen for T_g values. In the case of quenched sample A_f' we observe an intermediate behaviour and a double distribution of crystallites.

The transitions so far identified in this work appear clearly in the range $T = 120$–150°C from d.t.a. and d.s.c. analysis. A very important non-equilibrium zone is also observed up to $T = 130$°C with the abrupt decrease of the solvent retention volume in inverse gas chromatography corresponding to a different diffusion of the solute towards sorption sites which are no longer accessible. This phenomenon, probably due to the penetrability of the solute is induced by the mobility of the chain segments of the product. The variation of specific volume of the material, which decreases quickly in this range of temperature in dilatometry, confirms this transition.

CONCLUSION

The transitions of poly(allylbenzene) identified in this work are related to the amorphous and to the crystalline parts of the polymer, but also to zones for which transitions appear near 120–150°C, probably connected with a structural re-arrangement of the polymer.

Some small variation of temperature of the transitions was observed depending on the techniques used, keeping in mind that the experimental conditions influence the results[10,11] either for the glass transition or for melting[12].

As these transitions are related to relaxation phenomena, in an subsequent paper[13] we will deal with the electrical measurements on poly(allylbenzene).

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