Thermochimica Acta, 234 (1994) 95–101
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01502-T

Analysis of the thermal properties and motion in crystalline *trans*-1,4-poly(butadiene) [1]

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(Received 26 November 1992; accepted 7 May 1993)

Abstract

A new analysis of the disordering transition of semicrystalline *trans*-1,4-poly(butadiene) is presented, based on an improved calculation of the transition enthalpy from the crystal form **I** to the mesophase **II** (condis phase). In the past it had been overlooked that the experimental heat capacity starts to deviate more than one hundred kelvins below the peak temperature of the disordering transition temperature T_d from that contributed by the amorphous fraction and the crystal. An assessment of the additional entropy of disordering at lower temperature suggests that by the time the glass transition is reached on cooling, all the mesophase is converted to the fully ordered crystal form **I**.

INTRODUCTION

trans-1,4-Poly(butadiene) is perhaps one of the best-known flexible, linear macromolecules with a dynamic condis phase. A detailed review of its pseudohexagonal condis phase was given in 1988 [1]. Its heat capacity was analyzed first by Dainton et al. [2] and extended over the whole temperature range and linked to the cis isomer by Grebowicz et al. [3]. Two transitions, a low-temperature transition from the monoclinic crystal (form **I**) to the condis phase (form **II**) at $T_d = 356$ K ($\Delta H_d = 7.79$ kJ mol^{-1}) and the high-temperature transition to the isotropic melt $T_i = 437$ K ($\Delta H_i = 3.73$ kJ mol^{-1}), were first observed by Natta and Corradini [4] and interpreted as the existence of a mesophase with high conformational mobility. The listed equilibrium transition parameters were established by Finter and Wegner [5]. More recently it was shown that in the condis state

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[1] Dedicated to Hans Georg Wiedemann.

the commonly grown folded chain crystals can thicken to much more extended chain crystals [6], a property observed for several condis crystals [1]. The molecular motion in this interesting polymer has been studied by solid state NMR over many years [7–10]. In this paper, we will examine the extraordinary breadth of the crystal to condis-crystal transition observed by calorimetry.

In recent years it was observed that several polymers and low molecular mass compounds exist which have mesophases that do not fully order on cooling or have an extensive transition range [11–15]. The condis crystallinity of *trans*-1,4-polybutadiene will be shown to ultimately crystallize fully, but that is disordering transition can begin as low as about 210 K.

EXPERIMENTAL SECTION

Samples

No new heat capacity measurements were performed. Data taken by differential scanning calorimetry (DSC) [3] and adiabatic calorimetry [2] were reexamined. The original DSC measurements were carried out by heating at 10 K min^{-1} of samples of about 15 mg mass in N_2 atmosphere. The samples and reference materials were enclosed in nonhermetically sealed, matched aluminum cups. The temperature range of measurement was 220–450 K. The reexamined sample had 100% trans content and was crystallized from the melt at 320 K min^{-1} (sample A of ref. 3).

The adiabatic calorimetry involved measurements in the temperature range 20–340 K. The sample had a 96.2% *trans*-1,4- and a 3.8% 1,2-polybutadiene content, an intrinsic viscosity of 2.1 dL g^{-1} and was stabilized with 2,3-di-t-butyl-*p*-cresol. The mass of the sample studied was 27.318 g (sample B of ref. 2).

Calculation of the heat capacity of the solid

The theory of heat capacity is well documented in several publications from our laboratory [3–6]. Computer programs for these calculations have been described in detail [3, 4]. In short, the heat capacity contributions of the group vibrations are computed, making use of frequencies obtained from normal mode analyses fitted to IR and Raman data. After subtracting the group vibration contributions from the experimental heat capacity, the remaining contribution of the skeletal vibrations is fitted with the two characteristic temperatures of the Tarasov equation, θ_1 and θ_3. Reversing

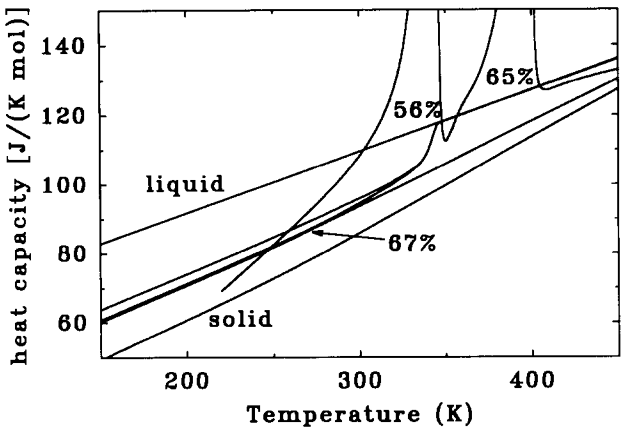

Fig. 1. Reexamination of the heat capacity of sample A1, measured by DSC [3].

this procedure, θ_1 and θ_3 and the group vibrations permit the computation of the vibrational heat capacity over a wide temperature range.

The details for the computation of the heat capacity of *trans*-1,4-polybutadiene are given in ref. 3. The characteristic temperatures θ_1 and θ_3 are 598.7 and 94.7 K, respectively. The computed data fit the recommended data bank results for the solid state from 20 to 280 K with an average error and a standard deviation of $+1.2 \pm 2.8\%$. Figures 1 and 2 display the computed heat capacity for the solid, together with the experimental DSC data. The DSC traces refer to heating of 100% *trans*-1,4-polybutadiene crystallized by cooling from the melt at 320 K min^{-1}. Also shown in the figures is the average heat capacity of the liquid polymer and lines computed for the expected heat capacities for the semicrystalline samples,

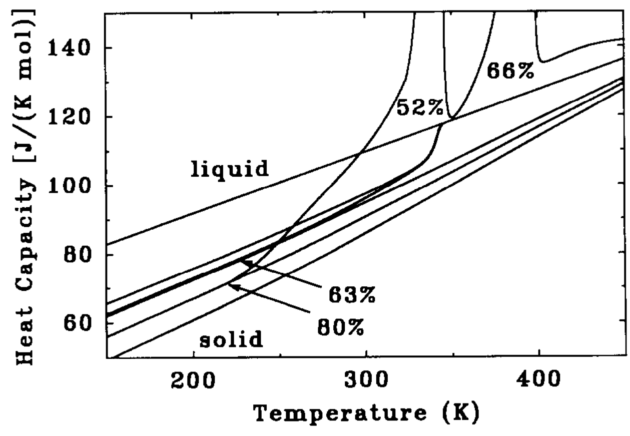

Fig. 2. Reexamination of the heat capacity of sample A1, measured by DSC, a second measurement [3].

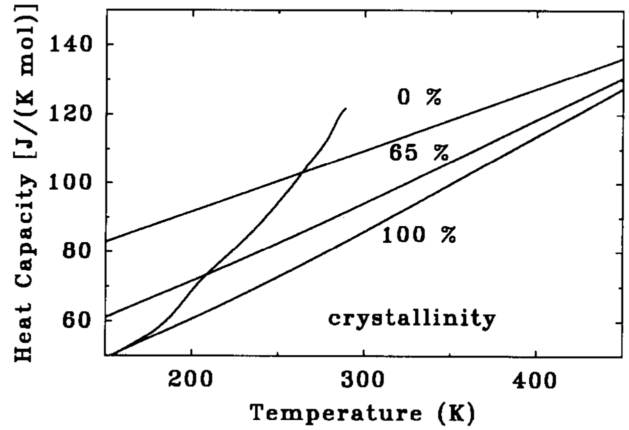

Fig. 3. Reexamination of the heat capacity of sample B measured by adiabatic calorimetry [2].

obtained by adding the proper fractions of solid and liquid heat capacities. The crystallinity for this calculation was derived from the measured heat of isotropization, ΔH_i.

Figure 3 shows a similar plot of the more limited adiabatic calorimetry [2]. As common in semicrystalline polymers, the glass transition for the amorphous portion of the polymer is rather broad. The midpoint of the increase in heat capacity is observed at about 190 K (T_g) [2]. The 65% crystallinity line in Fig. 3 is drawn as a guide for the expected heat capacity of a semicrystalline sample. In this case the heat of isotropization was not measured, i.e. the crystallinity is now known. The glass transition is in this sample somewhat more distinct. The overall shape of the measured heat capacity curve is similar to those of Figs. 1 and 2.

The new evaluation of the heat of disordering, ΔH_d, was done as follows: As a first approximation the liquid heat capacity was taken as the baseline of the disordering peak, similar to the earlier analyses [3]. The assumption of equal heat capacities in both phases has proven acceptable for several other mesophases (C_p(condis crystal) = C_p(liquid)). The liquid heat capacity intercepts the experimental line in Fig. 1 at 304.4 K. To calculate a more realistic baseline, one takes the first approximation for the enthalpy of disordering (form **I** crystallinity, calculated from $\Delta H_d = 4.40$ kJ mol^{-1}, for 100% crystallinity $\Delta H_i = 7.79$ kJ mol^{-1}, $w_\mathrm{I}^c = 56.5\%$). The heat capacity of a semicrystalline sample with a crystallinity w_I^c is then given by

$$C_p = w_\mathrm{I}^c C_{p,\mathrm{solid}} + (1 - w_\mathrm{I}^c) C_{p,\mathrm{liquid}} \tag{1}$$

During the disordering transition the initial crystallinity w_I^c changes continuously, to reach the value of zero at the end of the low-temperature transition peak (since $C_{p,\mathrm{condis\text{-}phase}} = C_{p,\mathrm{liquid}}$). To assess the continuously changing baseline, one computes

$$C_{p,\mathrm{baseline}} = [w_{\mathrm{I}}^{\mathrm{c}}(T)]C_{p,\mathrm{solid}} + [1 - w_{\mathrm{I}}^{\mathrm{c}}(T)]C_{p,\mathrm{liquid}} \tag{2}$$

where $w_{\mathrm{I}}^{\mathrm{c}}(T)$ is calculated from the fraction of the disordering that has been completed at temperature T

$$w_{\mathrm{I}}^{\mathrm{c}}(T) = \frac{\int (C_{p,\mathrm{measured}} - C_{p,\mathrm{baseline}})\,\mathrm{d}T}{\Delta H_{\mathrm{d}}} \tag{3}$$

Iterations with this equation not only lead to fast self-consistent crystallinities $w_{\mathrm{I}}^{\mathrm{c}}$, but also closely similar crystallinities $w_{\mathrm{I}}^{\mathrm{c}}$ and $w_{\mathrm{II}}^{\mathrm{c}}$. The remaining differences are of the order of a few percent and well within the margin of error. The crystallinities for the experiments displayed in Figs. 1 and 2 converge, respectively, at values of 62.2 and 67.1% for phase **I** based on the new evaluation of the disordering transitions, and 65.2 and 66.5% for phase **II**, based on the isotropization transitions. The earlier examination of the same data gave average crystallinities of 59% for the disordering and 68% for the isotropization and was interpreted as partial transition of phase **II** to phase **I** [2]. The new results prove the validity of the assumption that at sufficiently low temperature the crystallinity of form **I** is equal to the condis crystallinity. Since the samples of Figs. 1 and 2 were not measured through the glass transition range, it is not possible to judge whether the remaining deviation from the solid heat capacity line below 248 K is due to a rigid amorphous fraction of about 17% (see Fig. 2) or has to be taken as a broad glass transition with an upper limit being reached at 250 K. The adiabatic calorimetry on an isotopically less pure polymer in Fig. 3 reveals a more clearly defined glass transition, smoothly changing into the disordering transition at about 220 K.

DISCUSSION

The question in the original analysis [3], whether the rapidly cooled sample has a lower form **I** crystallinity than form **II** crystallinity can now be answered. The new analysis suggests that the residual material in the condis state that had not changed to form **I** at the beginning of the formerly used baseline, does so below 300 K. Reexamination of the DSC sample on heating reveals that the disordering transition starts immediately above the glass transition temperature. This makes the disordering transition more than 100 K wide. The broad disordering transition can be compared to other crystal to condis-crystal transitions. A similarly broad, and complete transition of about 150 K width was observed from the disordering of poly(tetrafluoroethylene) at room temperature (change of crystal form **II** to form **I**, the high temperature condis phase) [11]. Somewhat different is the behavior of *N,N'*-bis(4-*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD) [12]. Its low-temperature crystal (form K3) is still conformationally disordered. A broad increase in heat capacity from 250 to 390 K leads into the disordering transition and the broad heat capacity increase had to be interpreted as a glass transition. Without accounting for the heat capacity increase, only about 50% of the disordering expected for a fully ordered crystal could be accounted for. A similar amount of frozen conformational disorder that unfreezes over a broad temperature range was observed for polyethers containing longer methylene sequences and the semiflexible mesogen 1-(4-oxyphenylene)-2-(2-methyl-4-oxyphenylene)-ethane [13]. Some small molecules of a series of tetra-*n*-alkylammonium iodides show a similar disordering to a condis phase over a broad temperature range, outside of a sharp transition region [14]. Finally, the crystal to plastic-crystal transition of fullerene (C_{60}) also shows a slow beginning of a jump-like motion at about 100 K without increase in entropy, followed by a gradual increase in heat capacity, signaling beginning disorder at about 190 K, leading into a sharp transition at 256 K that yields the plastic crystals [15]. Broad transitions are thus a common occurrence with mesophases and must be studied by comparison of the measured heat capacity with that expected from a molecule that carries out vibrations only.

A direct link of motion and disorder in the solid state is possible by magic angle spinning cross-polarization (MAS CP) ^{13}C NMR. A number of investigations have been reported [8–10]. The results are in agreement with the here reported analysis down to 300 K, the lowest temperature analyzed above T_g [9]. The mesophase behavior was proven by the ^{13}C chemical shift values for the two different carbon atoms of *trans*-1,4-poly(butadiene). In the condis state the chemical shifts are very close to those of the isotropic melt (the differences are 0 and 0.6 ppm for the methene and methylene carbons, respectively), indicating the existence of considerable conformational disorder [8, 10].

CONCLUSIONS

It could be shown that the condis crystallinity and the crystallinity of *trans*-1,4-polybutadiene reach equal levels if compared at sufficiently low temperatures. It was necessary to develop a new calculation of the baseline for the integration of the broad disordering transition, making use of the heat capacity of the solid (vibration-only) and the liquid states. An iterative calculation then leads to reproducible values for transition enthalpies and crystallinities. If the sample is measured through the glass transition and the amount of the mobile amorphous fraction is known, the rigid amorphous fraction can be detected, even for samples without well defined peak onsets.

ACKNOWLEDGMENTS

This work was supported by the Division of Materials Research, National Science Foundation, Polymers Program, Grant DMR 92-00520 and the Division of Materials Sciences, Office of Basic Energy Sciences, US Department of Energy, under Contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

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