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PRECISION HEAT CAPACITY MEASUREMENTS FOR THE CHARACTERIZATION OF TWO-PHASE POLYMERS

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Structure sensitive thermal analysis results on linear macromolecules can be obtained when correcting measurements with heat capacity instead of "baseline" data. The ATHAS (Advanced Thermal Analysis) effort in heat capacities of crystals, glasses and liquids is described, and applied to the interpretation of microphase separated samples. Semicrystalline homopolymers, block-copolymers, and blends are to be discussed.

Heat capacities

All thermal analysis involves, at least indirectly, the measurements of heat capacity. Often this information is, however, discarded as "baseline" without utilizing the important, quantitative information. At ATHAS, our Advanced Thermal AnalysiS laboratory, we made it a goal to understand and collect heat capacities of linear macromolecules. The first step, which was concluded in 1980, was the collection of a data bank of all published information on heat capacities [1]. Data on heat capacities of about 100 macromolecules were collected and critically reviewed leading to sets of "recommended data" [1]. The next step involved the development of a "computation facility" which allowed the quick analysis of heat capacity data [2, 3]. This analysis is started with the pure vibrational heat capacity of solids. In short, heat capacities at constant pressure, C_p-data, are converted into heat capacities at constant volume, C_v. Next, all group vibrations are established. Group vibrations are the largely isolated vibrations of the side-groups of the macromolecular backbone [4] (such as the C—H bending, rocking, twisting, wagging and stretching vibrations in polyethylene). Their frequencies are found either from full vibrational analyses of the polymer crystal or the isolated chain, or from the interpretation of Raman and ir-spectra. The heat capacity contribution of the group vibrations is then computed using single Einstein terms for narrow frequency ranges or a box-distribution for broader ranges of frequencies. The total heat capacity contribution of the group vibrations is next subtracted from C_v

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(measured). The remaining heat capacity is due to the skeletal vibrations and is inverted in the temperature range to perhaps 200 K to a two-parameter frequency distribution, as suggested by Tarasov. The two parameters θ_1 and θ_3 are characteristic temperatures (frequencies) which describe the intra and intermolecular vibrational motion in the macromolecules. Their dependence on chemical structure and conformational variation is discussed, and then a complete heat capacity based on the frequency spectrum is calculated up to 1000 K. The basic "computation facility" is in place and described in two publications [2, 3]. Work on polyethylene [5, 6], polypropylene [7], all aliphatic polyoxides [6, 8, 9], and variously fluorinated and chlorinated polyethylenes [10, 11] is completed. Side-chain hydrocarbon polymers, polyesters, and several polydienes are under investigation. With the vibrational heat capacities known, an effort is made to correlate the measured heat capacities of the liquid phase [8]. Knowing the two limiting heat capacities, it becomes then possible to perform higher precision thermal analysis of non-equilibrium two-phase macromolecules, the main topic of this lecture.

Two-phase polymers

Two-phase polymers cover a wide range of important substances. Most of them do not reach equilibrium on phase separation and present thus a special challenge to thermal analysis.

The most common two-phase material is the semicrystalline polymer. Most analysis has in the past been limited to temperature and heat of transition determination. With data on the vibrational and liquid equilibrium state heat capacities known for a large number of macromolecules, it becomes now possible to have a more quantitative analysis. In the temperature range between the glass transition temperature T_g and the melting temperature T_m one can find both, positive and negative deviations from a purely additive heat capacity using a two-phase crystallinity model. These deviations indicate that the heat capacity is in this temperature range structure sensitive.

Positive heat capacity deviations have been linked with early melting of small crystals and rearrangement of crystals (i.e. polyethylene). Such deviations are thus latent heat contributions [5]. They can be identified by improving the sample crystal perfection and remeasurement. The deviations vanish. For polyethylene, positive heat capacity contributions which may occur as low as 270 K could be eliminated up to 410 K, less than 5 K below the equilibrium melting temperature [12].

Negative deviation of the heat capacity can obviously be caused by the reverse processes, namely crystallization related changes. More recently it was found that several macromolecules have a negative heat capacity contribution caused by a "rigid amorphous fraction." Polymers such as semicrystalline polyoxymethylene [9] and polypropylene [7] do not show full unfreezing at the glass transition of the amorphous fraction of the macromolecule. Instead, about half of the amorphous fraction retains a purely vibrational heat capacity, indicative of hindered mobility. The unfreezing of this "rigid amorphous fraction" may occur gradually up to the melting temperature, as in polypropylene, or it may not occur until the crystals melt, as in polyoxymethylene.

The transitions themselves can also be used for detailed structure-property interpretation. A detailed analysis of the expected equilibrium enthalpy and entropy changes for about 40 macromolecules was given earlier [13]. Severe reduction and partition into multiple transitions of the entropy of fusion could be established for mesophases (condis crystals) [14]. Typical examples are transpolybutadiene, polytetrafluoroethylene, polydiethylsiloxane, and polyparaxylylene. With detailed equilibrium data known, the non-equilibrium data can be inverted to free enthalpy distribution curves as soon as zero entropy production melting curves are available [15].

The glass transition is similarly able to characterize the polymer. A series of rather narrow backbone macromolecules such as polyethylene [16], polyoxymethylene [17], and polytetrafluoroethylene [18] seem to all show a rather broad glass transition with temperature ranges of 100 K or more which contrasts the normal 5 to 15 K range.

Another group of two-phase materials is represented by block-copolymers. Since in this case the phase-size is determined by the chemical structure, microphase separation is common. In this group of materials it was found that, again, the glass transition is a sensitive tool to detect microphase separation and to give quantitative information on the environment of the phase. From outright shifts of the glass transition, solubility can be deduced. From broadening towards higher temperature, one can conclude a rigid phase boundary, from broadening towards lower temperature, a moile phase boundary. The example analyzed in our laboratory involved poly(styrene-block-α-methyl styrene) [19].

A comparison with pure blends and copolymers shows that such broadenings and shifts of glass transitions are general phenomena [20]. They provide a special tool for characterization of two-phase materials, but are based on a quantitative assessment of the heat capacities ("baseline") of the solid and liquid. Perhaps, one of the most demanding applications was the analysis of liquid crystal macromolecules of the polyester type which show only a broad, gentle rise in heat capacity with a minor endotherm. By establishing the vibrational heat capacity, the glass transition could be separated [21].

Conclusions

A more quantitative thermal analysis is possible whenever heat capacities are established. Not only can equilibrium properties be tabulated [1, 13], but also, by making use of non-equilibrium measurements [15], it is possible to study thermal, mechanical and structural history [22]. Using these techniques coupled with the advanced computer data handling, computation and teaching techniques, a vigorous growth in thermal analysis is predicted for the future [23].

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Zusammenfassung — Ergebnisse der struktursensitiven thermischen Analyse von linearen Makromolekülen können erhalten werden, wenn die Messungen mit der Wärmekapazität anstatt mit „Grundlinien"-Daten korrigiert werden.* Semikristalline Hochpolymere, Blockpolymere und Mischpolymere werden diskutiert.

Резюме — Структурные данные для линейных макромолекул могут быть получены на основе результатов термического анализа при использовании точных измерений теплоемкостей, вместо данных базовой линии. Описана АТХАС попытка измерения теплоемкостей кристаллов, стекол и жидкостей, Что было использовано для интерпретации микрофазы отдельных образцов. Обсуждены гомополимеры, блок-сополимери и их смеси.

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* Die ATHAS-Datenbank wird bezüglich der Wärmekapazitäten von Kristallen, Gläsern und Flüssigkeiten beschrieben und zur Interpretation von in Mikrophase getrennten Proben herangezogen.