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Thermal properties of thermoplastic polymers: Influence of polymer structure and procedure of radical polymerization

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Experimental data prove a significant mutual interference between the chemical nature of the monomer and the particularities of the radical polymerization procedure which influences the thermal decomposition (depropagation) of the corresponding polymer. Results are presented for polystyrene, poly(methyl methacrylate), and poly(α-methylene-γ-valerolactone) which were made via different radical polymerization techniques (thermally self-initiated bulk polymerization at 80 °C, photoinitiated bulk and aqueous heterophase polymerization at 25 °C). Also, experimental data are presented after thermally annealing the polymers at 200 and 300 °C.

1. Introduction

Thermoplastic polymers are important commodities contributing in many ways to our daily life. They have to function properly within a given temperature range. Knowing the range of service temperature in which their chemical composition and physical properties remain unchanged is an important issue.

Typically, polymerization reactions are carried out under conditions with respect to temperature and monomer concentration where the propagation equilibrium is shifted almost entirely towards the product side. For radical polymerizations the enthalpy is governed by the heat release due to the transformation of the monomeric double bond into single bonds and the reaction entropy by the reduction of the number of individual molecules which is a factor in the order of the average degree of polymerization. Thus, most of the chain polymerizations are both exothermic and exoentropic. For two of the three monomers considered in this study, styrene and methyl methacrylate, the corresponding values of polymerization enthalpy and entropy are −73/−56 kJ/mol and −0.104/−0.117 kJ/(K mol), respectively [1]. Thermodynamically, polymerization is feasible as long as the negative enthalpy outweighs the product of temperature and entropy. However, this also implies that there is a temperature above which polymerization stops and depolymerization starts, the ceiling temperature (T_C). Thermodynamic treatment of the propagation equilibrium and the ceiling temperature shows that T_C is inevitably connected with a certain residual monomer concentration (M_C) [2,3]. T_C is for bulk polymerization of styrene and methyl methacrylate 310 and 220 °C, respectively [1]. Carrying out the polymerization at 25 °C (room temperature) one should consider M_C of about 10^{-6} and 10^{-2} M for styrene and methyl methacrylate, respectively [1]. The existence of something like the ceiling temperature implies, in general, that upon heating the propagation equilibrium can be shifted towards the monomer side and hence, it should be possible to decompose a polymer made via chain growth in its monomer units. Without knowing the thermodynamic fundamentals, the founding fathers of modern chemistry in the 19th century used destructive distillation to study the composition of natural organic materials such as caoutchouc and discovered a series of oils with different boiling points of which the lightest was named isoprene [4,5]. Very likely, this was the first systematic study of depolymerization. Today we know that caoutchouc, the natural rubber, is cis-polyisoprene.

The ceiling temperature is connected with the propagation equilibrium which involves radicals on both, the educt and the product side. Because of this, the existence of a ceiling temperature does not mean that a polymeric utensil made of polystyrene or poly(methyl methacrylate) inevitably begins to decompose already at or only from 310 to 220 °C on, respectively. The depolymerization reaction requires as first step the formation of radicals, typically via homolytic bond scission which can happen during any kind of

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mechanical or thermal stress randomly along the polymer chain. Homolytic bond scission, when it occurs, leads to the formation of two radicals and is the first step not only for the depolymerization to take place but, possibly also for a variety of other reactions depending on the particular chemical composition in the vicinity of the radicals.

Typically, the service temperature for a given polymer is much more governed by the glass transitions temperature (T_g) where it starts to soften. With increasing temperature, the atoms of a material fluctuate within a larger space causing a decrease in density (increase in volume) which makes any kind of reactions more likely to happen.

Among the many ways polymers can degrade this contribution deals almost exclusively with thermal degradation or in other words with that what happens during thermally stressing a polymer. Thermal stress may occur during production (mainly polymerization temperature), processing (either moulding, or extrusion, or mechanical shaping), application (service temperature), waste disposal, as well as waste treatment. In this study only thermoplastic polymers made via free radical polymerization are considered and neither thermosets nor polymers made via other polymerization mechanisms including controlled radical polymerizations. Also, we do not present data of broadband dielectric spectroscopy measurements which are frequently used to study changes in the mobility of polymers via studying the reorientation of dipoles in dependence on the frequency of an external electric field at different temperature [6].

There are numerous reports devoted to thermal analysis and characterization of polymers [7–10] highlighting various aspects of the influence of the structure of the polymer (its general chemical and physical structure) on thermal properties. However, to the best of our knowledge, no systematic study has been published so far dealing with the question whether for a given polymerization mechanism, here free radical polymerization, the particularities of the polymerization conditions (temperature, auxiliary materials, and dispersion state) influence the thermal properties and, if so, in which way and to what extent. The following polymerization conditions were screened in the present study with respect to: (1) temperature, either room temperature (25 °C) or 80 °C, (2) auxiliary materials, either none at all or only bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide) as photoinitiator, (3) dispersion state, either homogenous bulk or heterogeneous surfactant-free aqueous heterophase polymerization.

For our studies, we have chosen two well-known and well-characterized commodity polymers, polystyrene (PS) and poly(methyl methacrylate) (PMMA), and a rather untypical lactone-based polymer, poly(α-methylene-γ-valerolactone) (PMGVL). PMGVL was included because it can be considered as member of future polymers based on renewable feedstock [11,12]. The polymerization of α-methylene-γ-valerolactone has been reported already previously [13], utilizing different solution polymerization techniques such as radical, anionic, and group transfer polymerization. Also, photoinitiated radical bulk [14] and aqueous heterophase polymerization has been described [15,16]. Own studies confirmed that all free radical polymerization procedures (bulk, solution, aqueous heterophase polymerizations) and any kind of radical generation (photoinitiatian, thermal self-initiation, and free radical initiators) can be used [12].

The investigations of the present study include polymers as obtained after polymerization and samples which were thermally treated at 200 and 300 °C. The polymers were analyzed by means of elemental analysis (EA), Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (^{1}H NMR), size exclusion chromatography (SEC), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

2. Experimental information

2.1. Materials and methods

Styrene and methyl methacrylate (both of 99% purity from Sigma-Aldrich) were distilled under reduced pressure to remove inhibitors. α-methylene-γ-valerolactone (purity >96%, from TCI Europe) was freed from the inhibitor by passing through a column filled with aluminium oxide. The oil-soluble photoinitiator bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide) (**BAPO**) (Irgacure 819, Ciba Specialty Chemicals) was used as received. Water was taken from a SG purification system (Hamburg) with a conductivity of 0.055 μS cm^{-1}.

Details of the polymer synthesis via free radical polymerization have been described previously [12]. In brief, the following different free radical polymerization procedures have been employed. The procedures and recipes were kept simple in order clearly to understand the influence of the polymerization conditions. The first procedure is thermally self-initiated bulk polymerization of 5 g monomer at 80 °C as initial temperature (**TiB**). The second procedure is photoinitiated bulk polymerization of 5 g monomer containing 0.02 g of BAPO at 25 °C as initial temperature (**PiB**). The third procedure is surfactant-free photoinitiated heterophase polymerization with 5 g monomer containing 0.02 g of BAPO dispersed in water (**PiHetP**). The thermal and photoinitiated polymerizations were started by placing the glass vial containing the reaction mixture in an oil bath heated to 80 °C and in the middle between two standard fluorescent tubes (Osram L 18W, light color 840, lumilux, cool white) separated about 30 cm, respectively. For all polymerizations, the reaction mixture was magnetically stirred with 400 revolutions per minute which for the bulk polymerizations slowed down and eventually stopped with increasing conversion. All polymerizations were allowed to run for 48 h in order to maximize conversion and to ensure almost complete BAPO decomposition. The monomer conversion is mainly restricted by the glass effect. After polymerization the samples were dried in a vacuum oven at minimum membrane pump pressure. Samples treated in this way were used for all subsequent investigations. The polymers were exerted to a thermal stress after polymerization in a heating oven under nitrogen atmosphere for 15 h at both 200 and 300 °C.

The dynamic thermal properties of the polymers were investigated by thermal gravimetric analysis (TGA) and a differential scanning calorimetry (DSC). TGA was performed with a TG 209 F1 (Iris or Libra, in nitrogen atmosphere) and DSC with a DSC 204 “Phoenix”/TASC 414/4 controller (heat flow, endotherm up) both from Netzsch (Selb, Germany). If not otherwise stated, heating/cooling rates were for both TGA and DSC 10 K/min and for the evaluation of DSC data the third heating curve was used assuring that the thermal history of the sample was removed. All transition temperatures refer to the midpoint in the transition region of the heat flow time curves. The thermal cycle for the DSC measurements involved the following steps: 1 – cooling from room temperature to −90 °C, 2 – heating from −90 to +90 °C, 3 – cooling from +90 to −90 °C, 4 – heating from −90 to 200 °C (for PS and PMMA)/300 °C (for PMGVL), 5 – cooling back to −90 °C, 6 – heating to 200 °C/300 °C, and 7 – cooling back to room temperature. At each target temperature there was a resting time of 5 min.

The molecular weight distributions were determined by size exclusion chromatography (SEC) in N-methyl-2-pyrrolidone (NMP) containing 0.05 M LiBr at 70 °C with 8 × 300 mm GRAM-100/1000-7μ column (PSS Mainz, Germany), Shodex RI-71 refractive index detector, UV-1000 detector, and P-100 pump (flow rate 0.8 ml/min) all from Thermo Separation Products. Molecular weight data were evaluated on the basis of PS and PMMA standards. PMMA standards