Thermal Degradation of Poly(methyl methacrylate): Condensed-phase Kinetic Model and Experimental Investigation

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Abstract

Studying the thermal degradation of polymeric materials is a key step towards a sustainable chemical industry and to improve fire safety. This work proposes a condensed-phase semi-detailed kinetic model in CHEMKIN format for poly(methyl methacrylate) (PMMA) pyrolysis, based on a consolidated functional groups approach. The reaction network is built following previous studies on PMMA and analogous small gas-phase methyl esters. The elementary kinetic parameters are obtained from high-accuracy gas-phase kinetic data, polymerization studies, and by comparison with other vinyl polymers. A dedicated experimental campaign is conducted to assess the role of the defects in the polymer microstructure on the degradation behaviour. The model is validated by comparison with the new experimental data and a comprehensive set of literature data in terms of characteristic degradation times and product yields, proving able to describe and predict the underlying physico-chemical phenomena with reasonable accuracy. This work lays the basis for deriving reduced models and assessing secondary gas-phase reactions, extending the CRECK polymer degradation framework. It represents an initial step toward designing recycling reactors and advancing fire simulation studies.

Introduction

Understanding the decomposition pathways of polymers is key towards implementation of thermochemical recycling, design of next-generation propellants, and control of fire spread dynamics [1]. Product distribution optimization, process/reactor design, and pollutant control largely benefit from fluid dynamics and chemical kinetic modelling tools, thus motivating the present work. Studying the thermal degradation of poly(methyl methacrylate) (PMMA) is of interest due to its high monomer selectivity and its role as a model compound to investigate fire dynamics. PMMA decomposes by a radical mechanism that is significantly affected by the synthesis route, resulting in a three, two, or single-step process [2]. Several hypothesis and experimental investigations have been proposed, but there is no

fundamental model that can explain the underlying physico-chemical phenomena. To cover this gap, this work proposes a condensed-phase kinetic model for PMMA thermal degradation, based on a consolidated functional group approach [3]. To understand the effects of the polymer microstructure on the mass-loss profiles, a targeted experimental campaign is performed on samples produced via free radical (FRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization, the latter minimizing bimolecular terminations, and hence head-to-head (HH) defects and vinyl chain ends (VE). The model is validated also with volatile distribution data.

Experimental Methodology

PMMA was produced in toluene at a concentration of 50% w/w with azobisisobutyronitrile (AIBN) as thermal initiator at an operating temperature of 90 °C. For FRP, AIBN was used at 0.6% w/w with respect to monomer and the reaction lasted 4 h. For RAFT, the AIB was used at 0.23% w/w and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid was used as chain transfer agent, with the reaction run for 24 h. The produced polymer was purified via precipitation in methanol to remove the solvent and monomer conversion was assessed with GPC and ^{1}H NMR analyses. Finally, thermogravimetric analyses were carried out with a temperature ramp of 10 °C/min for mass losses determination.

Kinetic Model

Following the functional group approach [3], the chain distribution is modelled through a small set of pseudo-species representative of the chemical moieties of the polymer. On the other hand, a high level of detail is employed to describe real species of interest such as methyl methacrylate (MMA), CO, CO_2 and H_2. The pseudo-species introduced are distinguished in mid- and end-chain moieties, where the latter release light compounds able to evaporate (e.g., MMA). A radical depolymerization is considered for the liquid-phase reaction [2], while kinetic parameters are derived from previous literature investigation and analogy to gas-phase reactions [3]. The model accounts also for the presence of HH configuration and impurity weak links introducing the corresponding species and reaction classes.

Results and Discussion

Fig. 1 shows the model validation with new and literature experimental data on mass-loss profiles (left) and MMA yields (right). The model captures the effects of synthesis method on thermal degradation. Commercial PMMA, modelled defect-free, shows a single degradation step due to its stabilized structure. FRP-PMMA degrades at lower temperatures because of strained HH defects. RAFT-PMMA shows intermediate behaviour, as its synthesis process reduces but does not eliminate these defects. Considering volatile yields, the model captures the selectivity to unzipping and side-decomposition products (CO, CO_2, and short alkenes), although high uncertainty is involved in both the physical model and lab-scale fluidized bed

reactors employed for the experiments [5–7].

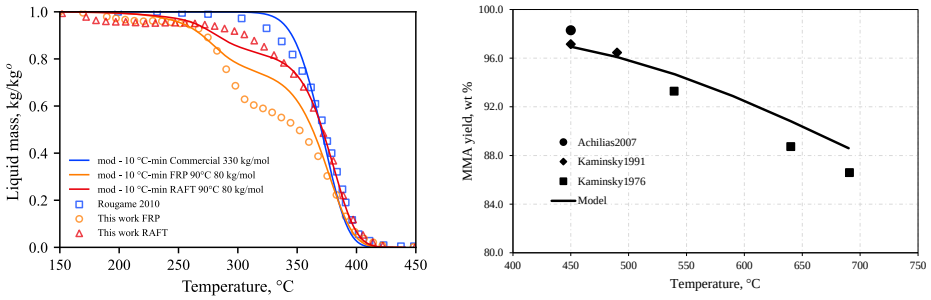

Figure 1. Comparison of PMMA experimental data (marks) and model predictions (line) for: left) mass-loss profiles [4], right) volatile yields [5–7].

Conclusions

The present work proposes a semi-detailed kinetic model describing thermal degradation of PMMA, validated with new and literature TGA and GC-MS experimental data, proving its capability in describing PMMA degradation from various sources and its high monomer selectivity. The model will be complemented by defining thermochemistry and secondary gas-phase reactivity.

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