

A Bench-Mark Method for the Evaluation of Co-Monomer Reactivity during Polyesterification using DSC with Micro Batch Reactors

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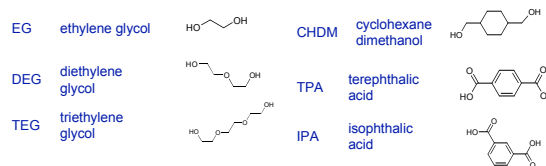
Introduction

- PET (poly(ethylene terephthalate)) is formed by step-growth polycondensation from ethylene glycol (EG) and terephthalic acid (TPA)
- The synthesis of PET requires two reaction steps
- The first step is polyesterification of TPA with EG, forming a short-chained prepolymer
- The second reaction step is polycondensation, in which a transesterification reaction takes place in the melt phase
- Esterification reactions occur during melt phase polycondensation, solid state polycondensation (SSP), and extrusion processes due to a significant concentration of carboxyl end groups
- As an equilibrium reaction, esterification is always accompanied by the reverse reaction being hydrolysis
- The esterification rate influences process time together with quality parameters of the polymer

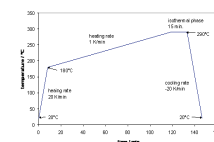
- PET properties can be modified by incorporation of co-monomers
- Typical co-monomers are isophthalic acid (IPA), 2,6-naphthalene dicarboxylic acid (NDC), cyclohexane dimethanol (CHDM), or diethylene glycol (DEG)
- Like the monomers, the co-monomers are diols or dicarboxylic acids and their reactions with TPA and EG follow the principal mechanisms of polyesterification and transesterification
- Very few data on reactions with co-monomers have been published so far, and it may be assumed that the same mechanisms and catalysis concepts should hold
- Nevertheless, it has been observed that co-monomers influence overall reaction rates significantly. This may in part be due to a reduced reactivity which could be a consequence of steric and electronic effects or of the influence of co-monomers on the mobility of functional groups

Experimental Methods

- Temperature programmed DSC (Netzsch, DSC 204) has been used to gain information on the reactivity of different PET co-monomers
- Tiny sealed gold plated pressure vessels with a volume of 27 μ l were used as reactors
- Three linear heating rates comprising 0.2, 0.5, and 1.0 K/min were applied between temperatures of 180 and 290°C
- The polyesterification of two carboxylic acids (TPA and IPA) with 4 diols (EG, DEG, TEG, CHDM) was investigated
- The initial molar ratios were 1.0, 2.2, and 10 mol_{diol}/mol_{dicarboxylic acid} with different particle sizes of the dicarboxylic acid
- Formal kinetic data were calculated by multivariate regression taking into account three heating rates for each individual combination of monomers



Compound	T_m / °C	$\Delta_m H$ / J/g
Biphenyl	69.2	120.4
Benzoic Acid	122.3	147.3
RbNO ₃	164.2	26.6
KClO ₄	300.8	104.9
Ag ₂ SO ₄	426.4	51.7
CsCl	476.0	17.2



Tab. 1: Compounds with their melting temperature and melting enthalpy used for DSC calibration

Fig. 1: Temperature-time profile for DSC runs, here with a heating rate of 1 K/min in the temperature range of the reaction

Results

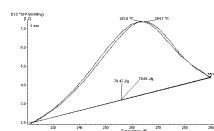


Fig. 2: Typical DSC results for repeated experiments, here for the polyesterification of TPA and EG at a heating rate of 1 K/min

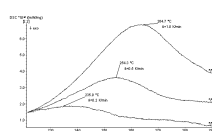


Fig. 3: DSC results for the polyesterification of TPA with EG; molar ratio EG/TPA: 1.0; heating rates: 0.2, 0.5, and 1.0 K/min

Acid	Diol	molar ratio	h / K/min	T_{max} / °C	$\Delta_m H$ / kJ/mol
TPA	EG	1.0	0.2	242	38.1
TPA	EG	1.0	0.5	254	30.7
TPA	EG	1.0	1.0	265	24.2
TPA	EG	2.2	1.0	261	49.1
TPA	EG	10	1.0	238	33.7
TPA	DEG	2.2	1.0	272	45.0
TPA	TEG	2.2	1.0	274	33.6
TPA	CHDM	2.2	1.0	266	33.0
TPA	EG/DEG	2.2	1.0	266	40.5
IPA	EG	2.2	1.0	219	23.6

Tab. 2: Overall heat of reaction (based on moles of dicarboxylic acid) and maximum peak temperature for the polyesterification of different dicarboxylic acids with different diols

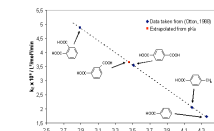


Fig. 4: Esterification rate constant as function of the pKa value of the dicarboxylic acid. Data taken from [2] (diamonds) and estimated rate constant for IPA from its pKa value (square)

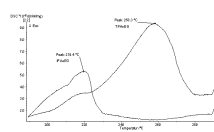


Fig. 5: DSC results for the polyesterification of TPA with EG and of IPA with EG, respectively, at an initial molar of 2.2 and a heating rate of 1.0 K/min

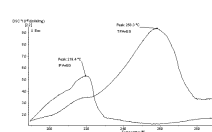


Fig. 6: DSC results for the polyesterification of TPA with EG, DEG, TEG, and CHDM, respectively, at a molar ratio of 2.2 and a heating rate of 1.0 K/min

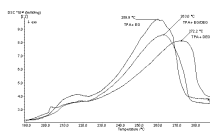


Fig. 7: DSC results for the polyesterification of TPA with EG, EG/DEG, and DEG, respectively, at a molar ratio of 2.2 and a heating rate of 1.0 K/min

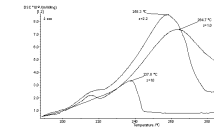


Fig. 8: DSC results for the polyesterification of TPA with EG at three different molar ratios diol / dicarboxylic acid of 1.0, 2.2, and 10, respectively, at a heating rate of 1.0 K/min

Conclusions

- Bench-mark information on the individual reactivity of co-monomers or the impact of process parameters like the molar ratio diol / dicarboxylic acid can be gained in short time and at low costs employing a commercial and medium sensitive DSC equipped with closed pressure vessels
- The shift of the maximum of the endothermic peak directly indicates the reactivity of the involved compounds respectively the influence of co-monomers, initial molar ratio, and process temperature on the polyesterification rate
- Formal kinetic data for the polyesterification can be derived from multivariate regression using the results from DSC experiments with at least three different heating rates
- The results of the kinetic models indicate the necessary adjustment of process time when recipes or process parameters are changed

References

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