

Towards a better understanding of the cosolvent effect on the low-temperature glycolysis of Polyethylene Terephthalate (PET)

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Poly(ethylene terephthalate) (PET) is the most diffused condensation polymer worldwide (Lase et al., 2023). The combined mechanical and chemical properties of this material allow its application in the production of bottles, trays and flexible packaging, as well as in the textiles industry. According to Plastics Europe (2022), the world PET production amounted to 24.2 million tonnes (Mt) in 2021, from which the EU27+UK region demanded 5.1 Mt. From this, merely 21% was recycled in 2020 and used in food and non-food packaging as well as in the fabrication of monofilament and fibre products (Eunomia, 2022). The largest part of the recycled PET fraction consists of clear and light blue bottles, primarily due to the lack of widespread recycling approaches for the more complex PET waste streams (Grant et al., 2022).

As the waste derived from PET use increases along with the worldwide production of the material, it is urgent to develop cost-efficient and sustainable chemical recycling processes that yields monomers with virgin-like qualities. However, most process reported in both the patent and scientific literature have not reached commercial scale due to their lack of economic profitability as consequence of factors such as the operation at harsh conditions and uses toxic substances (See Table 1).

Table 1. Exemplary reaction conditions of different glycolysis processes reported in literature.

EG:PET	Yield (%)	T (°C)	Time (min)	Catalyst	Ref.
12.6	88	190	100	Si-TBD	(Fehér et al., 2022)
15	91	180	120	TBD:MSA	(Jehanno et al., 2018)
16	78	190	210	TBD	(Fukushima et al., 2011)
7.6	80	196	60	Na ₂ CO ₃	(López-Fonseca et al., 2011)
13	86	180	90	Zinc Acetate	(Viana et al., 2011)

Herein, we report a process in which PET is totally depolymerized into bis(2-hydroxyethyl)terephthalate (BHET) with a yield of 88% by glycolysis at 65°C within 1 h in presence of Triazabicyclodecene (TBD) as organocatalyst after testing different molecular solvents as carriers (Figure 1). 1,3-Dioxolane was considered the most efficient solvent and used as green cosolvent carrier.

The cosolvent selection was made in base of the results obtained from the studies regarding the interaction of PET with a group of molecular solvents registered after a pre-screening stage. Conductor-Like screening model for realistic solvation (COSMO-RS) was applied for this. Since the polymer was not soluble in the solvents evaluated, the PET-solvent interaction was validated through solvent uptake experiments, DSC and SEM. THF and 1,3-dioxolane were the best solvents due to their ability to plastify and swell the polymer. Furthermore, the cosolvent to PET and EG to PET optimal molar ratios were determined. The effect of these parameters on the PET conversion and BHET yield was analysed also. Additionally, from the kinetic studies we concluded that the reaction behaves as a homogeneous system instead of a heterogeneous one although the reaction temperature is below the PET glass transition temperature (T_g). The last was attributed to the relaxation effect on the polymeric chains close to the surface of the sample as consequence of the swelling induced by the cosolvent. This phenomenon allows a better mass transport of the ethylene glycol and the catalyst into the polymer. The improved mass transport allows to perform the depolymerization of PET even below the T_g of the material. Indeed, we demonstrated that an heterogenous depolymerization process could be easily transformed into an homogenous process by an appropriate solvent selection. The Environmental impact of the proposed process is compared to the solvent-free counterpart and the results demonstrates that by using 1,3-Dioxolane, the glycolysis carbon emissions can be reduced up to 20% due to the increased energy efficiency. This process enables a viable recycling strategy of PET into its repetitive unit, contributing to the development of competitive chemical recycling solutions to reduce PET-derived pollution.

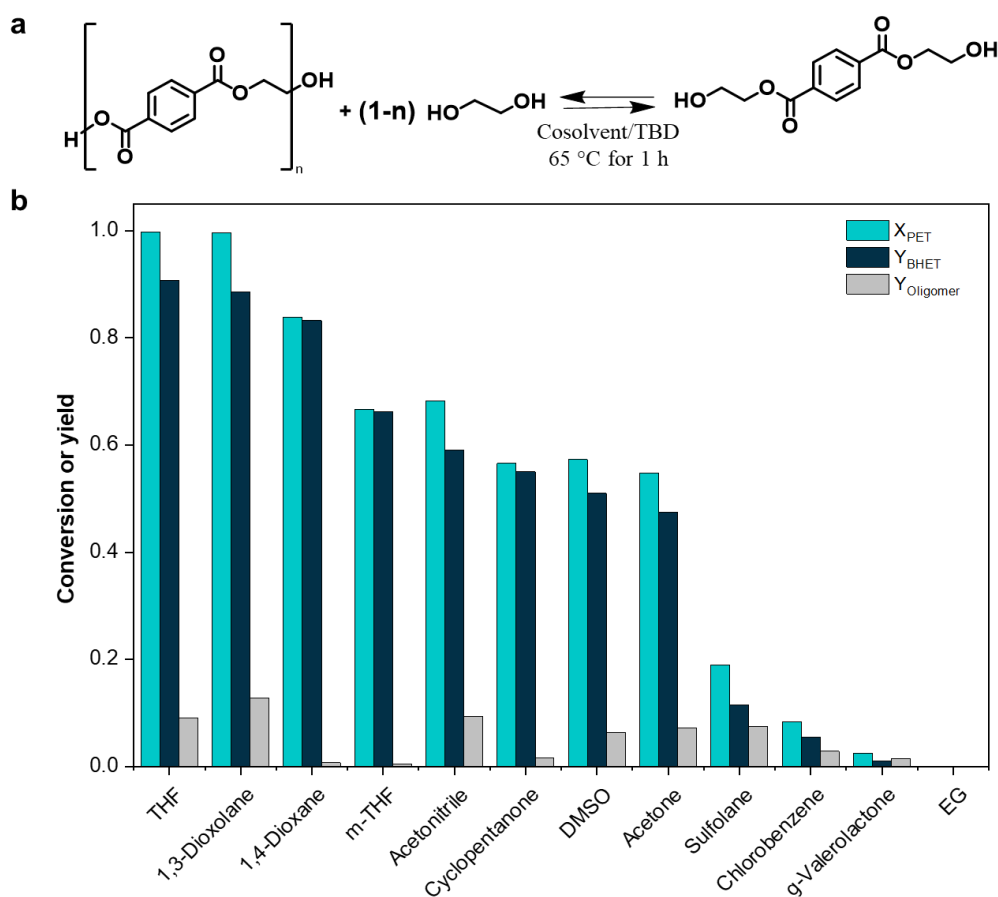


Fig. 1. (a) Glycolysis reaction scheme. (b) PET conversion and product distribution after 1 h of PET glycolysis with and without co-solvents at 65 °C using TBD as catalyst. The molar ratios of EG, co-solvent, and catalyst to PET monomer were adjusted to 3, 14, and 0.1, respectively.

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