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HIGH-TEMPERATURE RADICAL COPOLYMERIZATION OF DIBUTYL ITACONATE WITH N-BUTYL ACRYLATE, METHYL METHACRYLATE AND STYRENE

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The homopolymerization of itaconates results in relatively short polymer chains and low monomer conversions. To study whether copolymerization provides a more favorable result, dibutyl itaconate was copolymerized with n-butyl acrylate, methyl methacrylate and styrene. In addition to representing the most commercially preferred monomer families, these co-monomers were also chosen due to the differences in the secondary reactions that occur during polymerization at elevated temperatures. Experiments were conducted under semi-batch operating conditions at 110 °C with equal molar ratios of the co-monomer to dibutyl itaconate to enable direct comparison of the results. The impact of varying monomer compositions on polymer molecular mass distributions and polymerization rates was studied, with samples analysed using size exclusion chromatography and high-performance liquid chromatography.

Keywords:
copolymerization,
dibutyl itaconate,
monomer composition,
polymer molecular mass distribution,
semi-batch process

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1 Introduction

Commercial acrylic resins are typically produced by solution radical polymerization of methacrylates, styrene and acrylates, with the monomer selection based on both - material costs and the superior chemical and mechanical properties that they impart to the product. Free radical polymerization is versatile because it can polymerize many different monomers under relatively simple conditions. Due to the pursuit of sustainable development, there is a growing desire to replace these petroleum-based monomers with bio-based alternatives. As well as being amenable to polymerization, the bio-derived monomer substitute should match or even improve resin performance to be commercially beneficial (Li et al., 2016; Preusser and Hutchinson, 2016; Pirman et al., 2023; Pirman et al., 2024). One promising bio-based candidate is dibutyl itaconate (DBI), which is obtained by esterification of itaconic acid with butyl alcohol (Yu et al., 2020).

Common practice in commercial resin production is to continuously feed the monomers and initiator into the reactor pre-charged with solvent, operating under isothermal conditions at a temperature > 100 °C. Relatively low feed rates are used with this semi-batch operating strategy to facilitate high instantaneous conversions, such that the copolymer composition matches the comonomer feed composition over the entire course of the reaction. This feeding strategy also allows for better control of the heat generation compared to other reactor systems (Li et al., 2016; Wang and Hutchinson, 2008).

Our previous study has shown that DBI homopolymerization conducted under these operating conditions results in low monomer conversions and very low polymer molar masses, with the system limited by the increased importance of depropagation (Pirman et al., 2024). To study whether copolymerization provides a more favorable result, DBI was copolymerized individually with a monomer from each of the families typically used to produce acrylic resins: n-butyl acrylate (BA), methyl methacrylate (MMA) and styrene (St).

2 Experimental part

2.1 Materials

For experiments the following monomers were used: dibutyl itaconate (DBI; 99.3% purity, Novasol Chemicals), n-butyl acrylate (BA; 99% purity, Sigma-Aldrich), methyl methacrylate (MMA; 99.9% purity, Sigma-Aldrich) and styrene (St; 99.0% purity, Sigma-Aldrich). The solvent was butyl acetate (BAc; 99.5% purity, Sigma-Aldrich) and the initiator was 2,2'-azobis(2-methylpropionitrile) (AIBN; 98.0% purity, Sigma-Aldrich). Acetonitrile (99.9% purity, Honeywell), formic acid (98% purity, Merck) and tetrahydrofuran (THF; 99% purity, Fisher Scientific) were used for characterization. All chemicals were used as received.

2.2 Laboratory Semi-batch Experiments.

Semi-batch copolymerizations of DBI with BA, MMA and St were conducted at a Helios Resins laboratory under reaction conditions intended to mimic standard industrial operations using a Mettler Toledo OptiMax 1001 setup with a 1 L reactor vessel. The mass fraction of DBI in the feed was adjusted to keep the molar composition of the feed identical in all three copolymerizations. AIBN as the initiator was premixed with the monomer at a level of 2 wt % in relation to the total monomer, with the mixture dosed for 5 h at a constant rate into the stirred reactor vessel precharged with BAc solvent and maintained at 110 °C. At the end of dosing, the solvent level was 50 wt % of the total 200 g of solution, with the reactor kept at 110 °C for another 1 h before cooling. Multiple 1 mL samples were taken during the reaction.

2.3 High-Performance Liquid Chromatography (HPLC)/UV Analysis

A Waters HPLC system with separation module e2695 and XBridge C18 5 µm, 4.6 mm × 150 mm column was used for the determination of monomer conversions. The mobile phase was acetonitrile with 0.1% formic acid at different gradients throughout the 20 min run time at a 1 $\mathrm{mL \cdot min^{-1}}$ flow rate and 40 °C. Three parallels of samples and standards were prepared and filtered through a 0.45 µm filter. A calibration curve was made for all monomers and conversion was calculated based on the obtained quantity of either monomer in relation to the amount of monomer added up to the point of sampling. Gravimetry and gas chromatography were not used for the determination of conversion due to the high boiling point of DBI (284 °C).

2.4 Size-Exclusion Chromatography (SEC) Analysis

Samples were diluted in THF to achieve a polymer concentration of ~5 $mg{\cdot}mL^{-1}$ and passed through 0.2 μm nylon filters in preparation for measurement of the polymer molar mass distributions (MMDs) using an Agilent Technologies 1260 Infinity SEC instrument with an Agilent Technologies G1362A RI detector operating at 40 °C with a 0.3 $mL{\cdot}\,min^{-1}$ flow rate and using a single PLgel 5 μm Mixed-C column. Calibration was established using polystyrene (Poly(St)) standards in the range 580−2750000 $g{\cdot}mol^{-1}$. Based on repeat injections, the reproducibility of the measurements was within 10 %. The obtained polymer MMDs were relative to polystyrene and were therefore transformed to absolute values using Mark−Houwink parameters taken from the literature (Table 1).

Table 1: Mark-Houwink parameters for poly-DBI, poly-BA, poly-MMA and polystyrene (PS) in THF within the molecular weight ranges suitable for this study.

Polymer	K (10^{-3} ml g^{-1})	α
Poly(-DBI)	24.9	0.58
Poly(-BA)	12.2	0.70
Poly(-MMA)	14.3	0.71
Poly(St)	11.4	0.72

source: (Szablan et al., 2007; Wang and Hutchinson, 2010; Menges and Schmidt-Naake, 1998).

3 Results and discussion

3.1 Polymerization rate

The free monomer levels in the reactor, as determined using HPLC, were used to calculate overall monomer conversion over the course of the semi-batch polymerizations. Figure 1 compares the conversion profiles for the three monomer pairings, with each copolymerization system investigated at three different molar levels of DBI in the feed mixture. It is seen that the overall rate of conversion as well as the final conversion achieved decreases as the fraction of DBI in the feed is increased from 0.150 to 0.346 to 0.614. This result is explained by the influence of DBI depropagation on the system (Pirman et al., 2023).

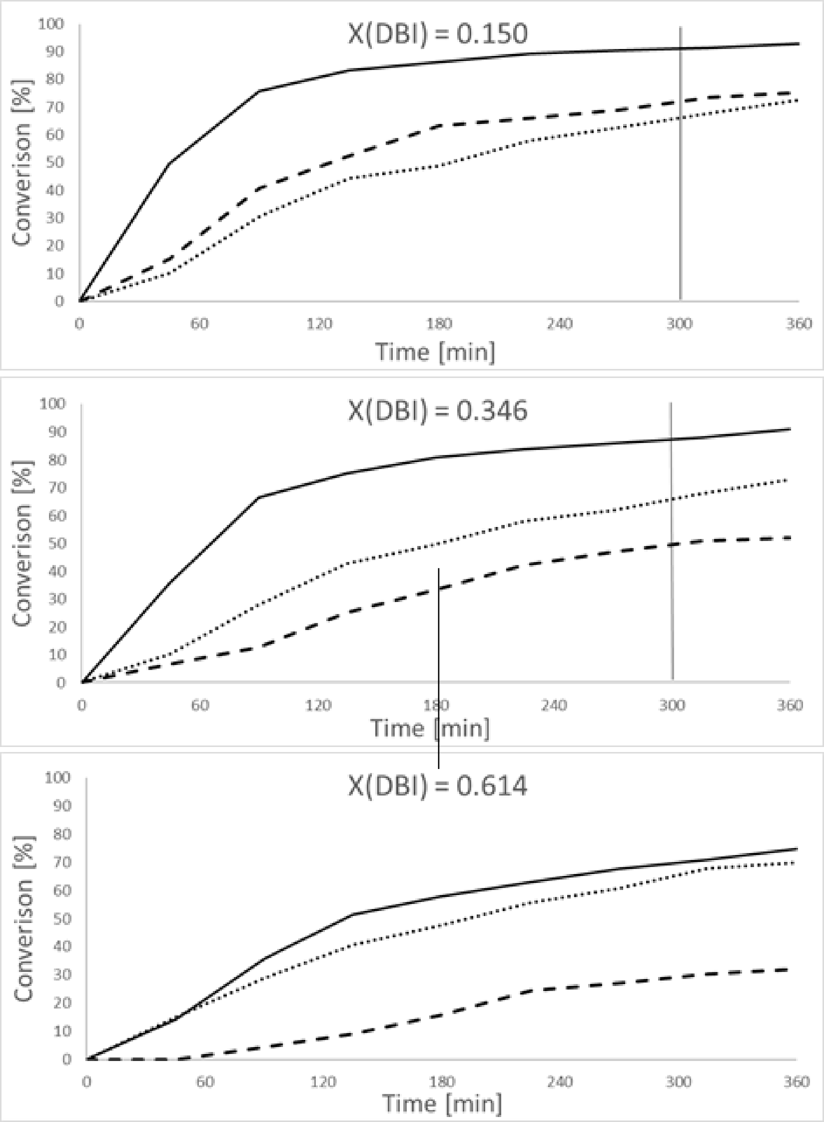


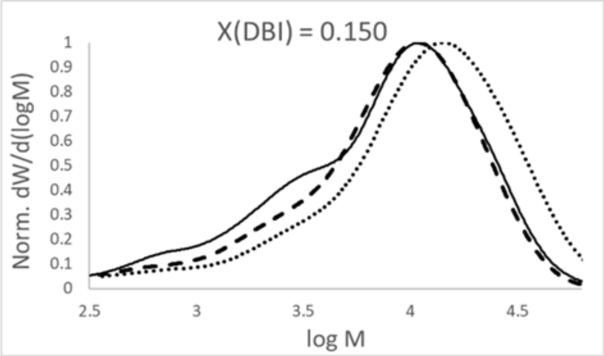
Figure 1: Experimentally obtained data for overall monomer conversion taken during the reactions. Copolymerization of DBI with BA (solid lines)/MMA (dashed lines)/St (dotted lines) for various amounts of DBI (mole fraction). The vertical line represents the end of dosing.

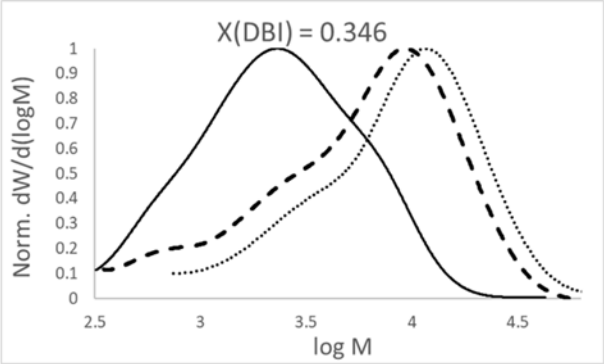
Source: own.

For all feed compositions, the highest monomer conversion is achieved with the acrylate (BA) as comonomer, with only the highest DBI level leading to an observable decrease in the final BA/DBI conversion due to the influence of depropagation. At the lowest DBI level (0.150), the rate of conversion is higher for DBI/MMA than DBI/St, a result consistent with the known higher homopolymerization rates of MMA compared to St. However, the DBI/St rates and final conversions are higher when DBI level is increased, indicating the increased importance of depropagation for the methacrylate-itaconate pairing. Another interesting finding is that copolymerization DBI/St at all three fractions of added DBI leads to similar final conversion (~ 70 %).

3.2 Polymer MMDs

Figure 2 shows the MMDs measured for the final polymer samples at the end of the reaction, demonstrating how the comonomer choice and the DBI level affects the copolymer product.





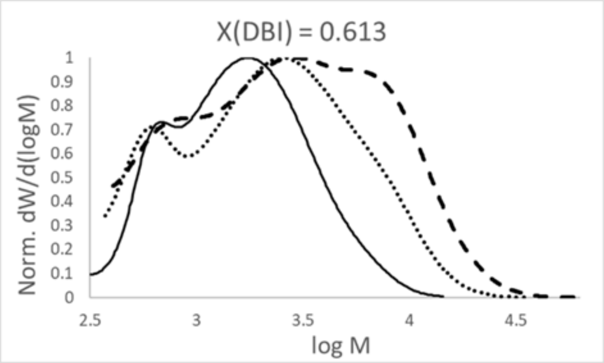


Figure 2: Experimentally obtained data for MMDs – final samples. Copolymerization of DBI with BA (solid lines)/MMA (dashed lines)/St (dotted lines) for various amounts of DBI (mole fraction).

Source: own.

According to Figure 2, it is evident that the greater the proportion of added DBI, the shorter the polymer chains on average. It is also easy to notice that at all three molar ratios, the polymer chains in the copolymerization of DBI/MMA and DBI/St are no longer compared to the copolymerization of DBI/BA, despite the higher rates of conversion observed for the DBI/BA system. This interesting result suggests that the influence of chain transfer mechanisms is higher for this copolymerization system, a result that must be studied further.

4 Conclusion

The comparison of the three DBI copolymerization systems provided some interesting findings and optimistic results showing the incorporation of bio-based monomers into copolymer formed under commercial operating conditions. However, it is necessary to limit the molar level of DBI, in order to produce polymers with sufficiently high molar masses at a reasonable rate. Although the copolymerization of DBI with BA had the highest rates, the polymer molar masses were lower than those measured for DBI/St and DBI/MMA. Based on these experiments, the optimal comonomer combination is dibutyl itaconate and styrene with 35 mol. % DBI, which is equivalent to slightly more than 55 wt. %. To more accurately determine the optimal proportion of DBI for copolymerization with St or other comonomers, additional experiments over a broader range of conditions are required, along with an evaluation of economic, environmental, and other factors that must be considered for commercial application.

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