Journal of Polymer Science

WILEY

JOURNAL OF
POLYMER SCIENCE

RESEARCH ARTICLE OPEN ACCESS

Synthesis of Poly(Itaconate)s With High Monomer Conversion Applying Emulsion Polymerization

S. Charlotte Fischer von Mollard[1,2] | Nico Ueberschaar[3] | Martin Schreiber[4] | Frank Kamphuis[4] | Stefan Zechel[1,2] | Martin D. Hager[1,2,5]

[1]Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Jena, Germany | [2]Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Jena, Germany | [3]MS Platform, Friedrich Schiller University Jena, Jena, Germany | [4]ACTEGA Terra GmbH, Lehrte, Germany | [5]Helmholtz Institute for Polymers in Energy Applications Jena (HIPOLE Jena), Jena, Germany

Correspondence: Martin D. Hager (martin.hager@uni-jena.de)

Received: 24 May 2024 | **Revised:** 15 August 2024 | **Accepted:** 4 September 2024

Funding: This work was supported by Bundesministerium für Ernährung und Landwirtschaft (2220NR070A and 2220NR070B).

Keywords: biobased polymers | emulsion polymerization | poly(itaconic acid esters) | radical polymerization | renewable polymers

ABSTRACT

Itaconic acid and its derivatives can be obtained from renewable feedstocks. However, there are only very limited applications of polymers containing itaconic acid so far. One limitation of the application of this polymer is that commonly utilized polymerization techniques lead to very low conversions of the corresponding monomers. Consequently, itaconic acid and its derivatives are generally considered difficult or poorly polymerizable monomers. The current study presents the improvement of the polymerization by applying an emulsion polymerization of itaconic acid esters, leading to very high monomer conversions with a residual monomer content of less than 1%.

1 | Introduction

Due to the depletion of petroleum and more environmental awareness, the synthesis of polymers using renewable feedstocks is getting more and more important [1–3]. Besides lactic acid, itaconic acid (IA) and its derivates are one of the most promising renewable monomers [4–6]. IA can be produced by fermentation of corn, rice starch, or lignocellulosic feedstock, which is not used for food, using many different fungi such as *Aspergillus terreus* [7, 8], *Pseudozyma antarctica* [9], *Ustilago maydis* [10], and *Aspergillus niger* [11]. The former fungus is utilized for the commercial production of IA, which is more than 80,000 tons per year [8, 12].

IA can also be applied as a building block for the synthesis of polyesters in polycondensation reactions [13–15]. Furthermore, it is also an alternative to methacrylate- and acrylate-based monomers. Thus, IA and the corresponding esters, the itaconates, can be used as comonomers in radical polymerizations [3, 16–20]. Depending on the composition of these copolymers, the applications range from superabsorbents [21] to thickeners [22] or coatings [23]. It is also possible to equip the ester groups with other polymerizable functionalities [24].

The radical homopolymerization of IA and its derivates is highly challenging, and thus, these homopolymers or copolymers with the IA-esters are nearly not accessible on a larger scale. In particular, IA has a rather low reactivity and tends to side reactions, such as decarboxylation [18, 25–27]. Furthermore, the conversions are often relatively low, leading to low yields. Nevertheless, there are some first reports on the radical polymerization of IA and its derivates [28]. In the case of the free-radical polymerization (FRP) of IA, the reachable monomer conversions are low to medium (32% [26] up to 84% at 60°C after 142 h in dioxane with azobisisobutyronitrile (AIBN) as the initiator [25]). The molar masses obtained under these conditions are rather low, combined with high dispersities [25, 26, 29]. The synthesis of IA oligomers in water with V-50 as initiator has already been

https://doi.org/10.1002/pol.20240414

reported. The monomer conversion was above 90%, but the molar mass obtained was rather low [30].

In contrast, the FRP of IA esters in bulk leads to higher conversions, although the molar masses tend to be lower here as well [18, 25, 26, 31]. For dibutyl itaconate (DBI), a conversion of 81% can be achieved with FRP in bulk after 20 h at 25°C with dimethyl 2,2′-azobisisobutyrate (MAIB) as the initiator [32].

During the atom transfer radical polymerization (ATRP) of IA, complexes are formed between the CuCl catalyst and the deprotonated monomer, which disrupts the control over the polymerization [33]. In contrast, the ATRP of the uncharged cyclic itaconimides leads to high polymerization rates [34]. The reversible addition-fragmentation chain transfer (RAFT) polymerization of IA esters leads to high conversions (up to 99%) and molar masses, as well as narrow molar mass distributions. However, the reaction time of the RAFT polymerization was 160 h, which is very long and, therefore, high-energy consuming [35]. In general, the esters and the anhydride of IA are easier to polymerize *via* different radical polymerization reactions compared to the acid. Nevertheless, even for the IA esters and the itaconic anhydride, the conversions are relatively low, the reaction times are rather long, and the molar mass are mostly low and the molar mass distributions are very broad [28, 31].

Enabling a potential industrial application of poly(itaconic acid) derivatives, the synthetic route toward these materials must also be applicable on a larger scale. Within this context, emulsion polymerization offers one possibility. Due to the great potential of emulsion polymerization, emulsion polymerization has developed as a method for synthesizing a wide variety of polymers. Nevertheless, there are many reaction parameters, such as the stirring geometry, which make it difficult to transfer the reaction to other reaction vessels. If the reaction parameters change, the properties of the polymer may also change. Therefore, optimization and online control of the reaction is necessary [36]. Emulsion polymerization is receiving a lot of attention in research due to its many possibilities, especially since water is in demand as a green solvent in terms of sustainability [37]. However, no homo-polymerization of IA using emulsifiers reaching high conversions has been described in the literature so far, whereas the copolymerization of IA esters with acrylic acid, acrylic acid esters and acrylic acid amides is well reported [3, 17, 18, 38]. A first example of the emulsion polymerization of IA esters is reported in the literature. However, the conversion of this reaction is low (below 13%) [39].

Within this context, we present a new approach for the emulsion polymerization of IA esters reaching high conversions, yields and higher molar masses. For this purpose, different reactions conditions have been studied systemically.

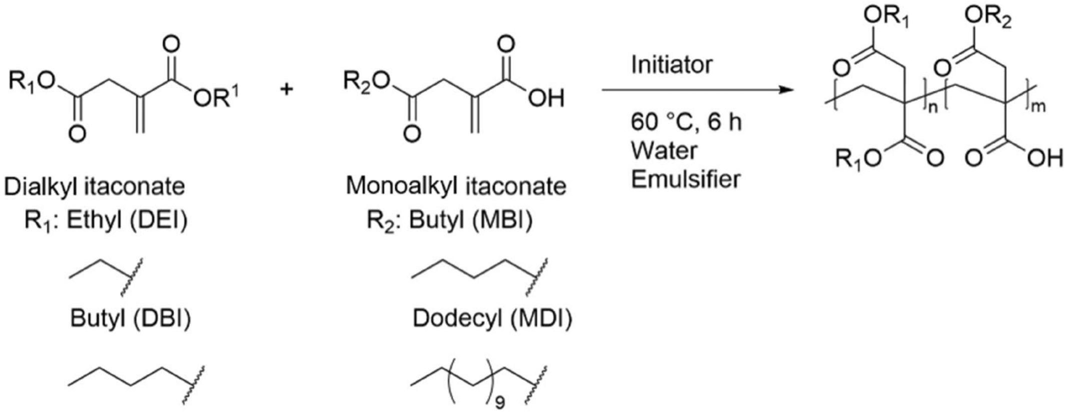
2 | Results and Discussion

The aim of our study was to establish an emulsion polymerization of IA esters with high monomer conversions and yields. The intended monomers were the dialkyl itaconates (diethyl itaconate [DEI] and DBI) as well as the monoesters (monobutyl itaconate [MBI] and monododecyl itaconate [MDI]) (see Scheme 1). All monomers were selected due to good accessibility either commercially or *via* a one-step synthesis.

The two diesters should be utilized in copolymerizations with the monoesters. Hereby, the ratio of the comonomers was always set to 95:5 (diester:monoester). Furthermore, the homopolymers of the diesters should be synthesized for comparison.

2.1 | Initiator Screening

To establish the emulsion polymerization of the itaconates, first the effect of various water-soluble initiators was examined. Therefore, four different water-soluble initiators have been utilized: potassium persulfate ($K_2S_2O_8$) and the three different azoinitiators 4,4′-azobis(4-cyanopenatonic acid) (ACPA), 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044), and 2,2′-azobis(2-methylpropionamidin)dihydrochloride (V-50). The initiators used differ in their decomposition temperature, whereby ACPA features the highest decomposition temperature. Here, the 10-h half-life decomposition temperature is 69°C [40], whereas it is 60°C for potassium persulfate [41], 56°C for V-50 [42], and 44°C for VA-044 [40]. The applied initiators are either cationic or anionic. Compared to the emulsifier and the acid groups of the polymer; however, the initiator only has a very small influence on the overall charge of the polymer particle due to its low content in the mixture. For other emulsion polymerizations, it has been reported that the opposite



SCHEME 1 | Schematic representation of the emulsion polymerizations of itaconates.

charge of the initiator and the emulsifier did not affect classical emulsifiers (in contrast to polysoaps) [43].

All four initiators were screened for the polymerization of DEI and MBI (see Table 1) and two different initiator concentrations have been applied. The polymerizations have been performed in water at 60°C for 6 h utilizing sodium dodecyl sulfate (SDS) as emulsifier (for details see the experimental part). All reactions performed were characterized according to the same protocol.

The yield of the polymers was studied by weighing the obtained dry polymer after purification *via* dialysis (1 kDa). Hereby, any residual monomer, small oligomers, or other contaminations, such as solvents, are removed to determine the yield of the polymers only. We aimed at high yields of high molar mass polymers with only a lower content of smaller oligomers and a low content of residual monomers. The yields of these polymerizations are shown in Figure 1.

Furthermore, the molar mass and the dispersity of the purified polymers were determined *via* size-exclusion chromatography (SEC). The measurements are shown in Figures S2–S32. Hereby, the polymerization can be verified; however, the molar mass of the reactions is rather low, which is due to the poor polymerizability of IA esters. In the ^{13}C spectrum, a proportion of less than 5% of the chain transfer, which will reduce the molar masses, can be recognized. This content is a rather low proportion compared to the literature. There, a proportion of 15% is reported in the bulk, and with the addition of a Lewis acid, the proportion is reduced to 5% [44, 45].

For only a few polymers, an interesting feature can be observed: they feature a bimodal molar mass distribution. In particular, this phenomenon can be observed for polymers with low yields, such as **P8**. In general, bimodal distributions in emulsion polymerizations can be caused by various factors. The more hydrophilic comonomer MBI could presumably lead to partial polymerization in solution, which would cause the bimodal distribution.

For all polymers with a yield of more than 10%, the acid content was determined by titration as well. The content was found to be about 5% (Table S4), as it could be expected due to the utilized monomer composition (95:5). The results are summarized in Table 1.

Potassium persulfate is a frequently used initiator for the emulsion polymerization, for example, of styrene [46]. However, the standard amount of potassium persulfate (**P1**) is not sufficient to obtain any relevant yield (0.9%). Only the double amount of this initiator leads to an improved yield (**P2**: 24.1%, $M_n = 78{,}400\,\mathrm{g\,mol^{-1}}$). The observed behavior can be explained by the accelerated decomposition of the potassium persulfate due to an interaction of the free acid of the monoester with the initiator, requiring a higher amount of initiator for sufficient polymerization [47].

Since azoinitiators are bulkier compared to potassium persulfate, the interaction with the acid should no longer take place or at least should be reduced [47]. Therefore, three different

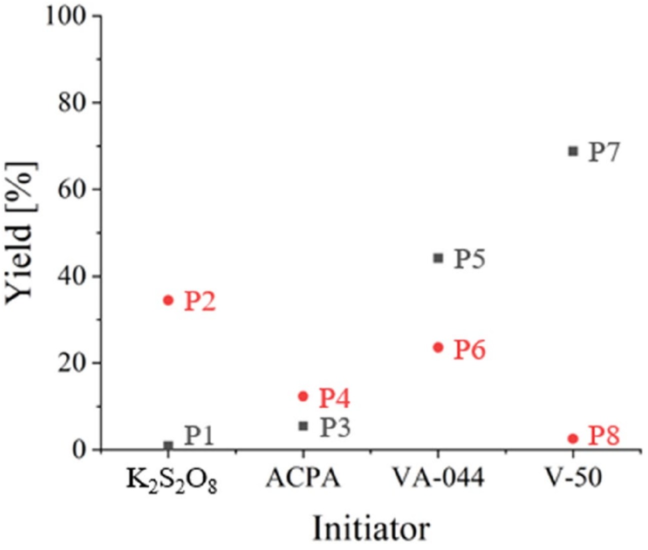


FIGURE 1 | Overview of the obtained yields of the emulsion polymerization of DEI with 5% MBI with different initiators as well as different amount of these (black—lower amount, red—higher amount). The composition of the emulsions is described in detail in Table 1.

TABLE 1 | Composition and analytical results of **P1**–**P8**.

Polymerization	Diester type	Monoester type	Initiator [mmol]	Initiator Type	Emulsifier [g]	Emulsifier Type	M_n [g mol^{-1}]^a	M_w [g mol^{-1}]^a	$Đ^a$	Yield [%]
P1	DEI	MBI	0.225	$K_2S_2O_8$	0.5	SDS	43,000	159,600	3.70	0.9
P2	DEI	MBI	0.45	$K_2S_2O_8$	0.5	SDS	78,400	353,500	4.51	24.1
P3	DEI	MBI	0.225	ACPA	0.5	SDS	19,800	63,500	3.21	5.5
P4	DEI	MBI	0.45	ACPA	0.5	SDS	65,500	112,700	1.72	12.3
P5	DEI	MBI	0.225	VA-044	0.5	SDS	23,200	75,900	3.40	44.2
P6	DEI	MBI	0.45	VA-044	0.5	SDS	3500	29,300	8.44	23.6
P7	DEI	MBI	0.255	VA-50	0.5	SDS	187,000	1,367,000	7.31	69
P8	DEI	MBI	0.45	VA-50	0.5	SDS	234,200	975,800	4.17	3

^{a}Determined via SEC measurements (THF, PMMA-standard).

water-soluble azoinitiators, ACPA, VA-044, and V-50, were utilized, which differ in their 10-h half-life temperature as well as their charge. During the emulsion polymerization, it could be recognized that ACPA is not a suitable initiator for the polymerization of IA esters since reaction yield is well below 15% (**P3**: 5.5%). Even the double amount of ACPA is not sufficient to obtain any relevant conversion (**P4**: 12.3%). For ACPA, the molar mass M_n is about 19,800 gmol^{-1} (**P3**) and for the double amount of initiator, M_n was found to be 65.500 g mol^{-1}(**P4**).

In contrast, the application of VA-044 resulted in significantly higher yields of 45% (**P7**) with the standard initiator amount. If the initiator quantity was doubled, the reaction yields were lower. With VA-044 as the initiator, M_n decreases when the initiator quantity is increased. The molar mass M_n of the polymerization of **P5** with the standard amount of initiator was found to be 23,200 and only 3500 g mol^{-1} with the double amount of VA-044 (**P6**). As a result, a significant percentage of the yield is lost during dialysis due to the very low molar mass of the synthesized polymer.

Finally, V-50 was tested and was found to be also suited as the initiator. With a single initiator quantity, the yield is only slightly lower compared to VA-044 (**P7**: 69%). However, the yield when using twice the amount of initiator is significantly lower compared to VA-044 (**P8**: 4%). Since V-50 has a higher decomposition temperature than VA-044, there are less radicals in the reaction mixture, and the molar mass of the reactions is higher (**P7**, $M_n = 187{,}000$ g mol^{-1} and **P8**, $M_n = 64{,}500$ g mol^{-1}). The dispersity of the polymers obtained by V-50 is also significantly higher than that of VA-044 despite the good yield (**P7**: $Đ = 7.31$). This is probably also caused by the higher decomposition temperature.

The result of the initiator screening was that VA-044 was identified as the best working initiator for the selected copolymer, since the reactions resulted in higher yields and lower dispersities.

To test the transferability to the second dialkylitaconate, the polymerization has also been performed with the same conditions as DBI. The results of this synthesis are summarized in Table 2 and are displayed in Figure 2.

In general, the results are comparable to the polymerization of the DEI, **P1** to **P8**. The main difference can be found for the azo-initiators VA-044 and V-50. Comparing **P5** to **P11** (VA-044 as initiator), the yield of **P5** (44%) is slightly lower than the yield of **P11** (69%). With **P7** (69%) and **P12** (38%) (V-50 as initiator) it is the opposite. Depending on the monomer, either V-50 or VA-044 provides the better yield. However, since VA-044 works a slightly better overall, VA-044 was used as the initiator for further experiments.

2.2 | Emulsifier Screening

With VA-044 as a suitable initiator for both copolymers in hand, various emulsifiers were investigated. The interaction of polymer and emulsifier depends on various factors, such as the surface charge of the particle or the type of emulsifier [48]. This interaction has a major influence on the stability and, consequently, on the yield of the emulsion. For later potential applications of the synthesized emulsion, the emulsifier will also play a crucial role. For the first tests, SDS was a good surfactant; however, it is not yet known if there are other suitable emulsifiers IA esters. Consequently, various emulsifiers were tested. In addition to the previously utilized anionic SDS, another anionic emulsifier, as well as nonionic surfactants, were tested (Figure 3). Cationic surfactants have been excluded due to the anionic monoester.

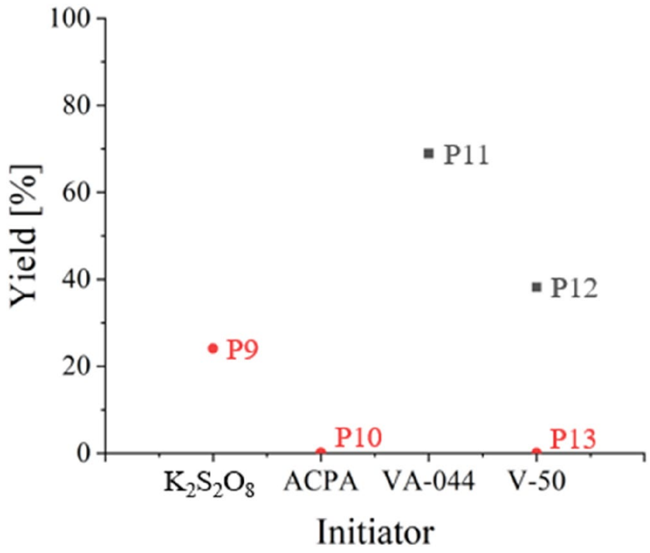


FIGURE 2 | Overview of the obtained yields of the emulsion polymerization of DBI with 5% MBI with different initiators as well as different amounts of these (black—lower amount, red—higher amount). The composition of the emulsions is described in detail in Table 2.

TABLE 2 | Composition and analytical results of **P9**–**P13**.

Polymerization	Diester type	Monoester type	Initiator		Emulsifier		M_n [g mol^{-1}][a]	M_w [g mol^{-1}][a]	$Đ$[a]	Yield [%]
			[mmol]	Type	[g]	Type				
P9	DBI	MBI	0.45	$K_2S_2O_8$	0.5	SDS	68,700	148,600	2.16	34.5
P10	DBI	MBI	0.45	ACPA	0.5	SDS	70,400	132,900	1.89	0.2
P11	DBI	MBI	0.225	VA-044	0.5	SDS	32,500	91,900	2.80	69.0
P12	DBI	MBI	0.255	VA-50	0.5	SDS	64,500	155.800	2.42	38
P13	DBI	MBI	0.45	VA-50	0.5	SDS	—	—	—	0

[a] Determined via SEC measurements (THF, PMMA-standard).

Dioctyl sodium sulfosuccinate (DOSS) is another anionic surfactant that has been utilized frequently as an emulsifier [49]. The nonionic surfactants used were Triton X-405 and a mixture of Span 80 and Tween 80 with a ratio of 9 to 91. This mixture has been selected on the basis of their hydrophilic–lipophilic balance (HLB) value, which describes the hydrophilic and lipophilic content of nonionic surfactants. The HLB value is calculated using the molar mass of the lipophilic part of the molecule M_l and the total molar mass M of the molecule. The scale ranges from 0 to 20 [50].

$$\mathrm{HLB} = 20\left(1 - \frac{M_l}{M}\right). \quad (1)$$

For an emulsion polymerization, this value should be between 8 and 18 [51]. For Triton X-405, the HLB value is 17.9 [52], which means that this emulsifier is relatively hydrophilic [51]. Consequently, Triton X-405 has already been applied for emulsion polymerizations [53, 54]. The HLB value of a 9:91 mixture of Span 80 and Tween 80 is 14 [55] and is, therefore, also according to literature a good emulsifier for emulsion polymerization [51]. Based on this, we chose this ratio for a detailed investigation.

For the investigation of the emulsifier, we applied polymerization in analogy to the polymerization of **P5** (**P14**, **P16**, **P18**) and **P11** (**P15**, **P17**, **P19**) and exchanged SDS by the other emulsifiers (see Table 3). Figure 4 clearly shows that the emulsion polymerization yields differ significantly when Triton X-405, Span 80 and Tween 80 (9:91), and DOSS are utilized instead of SDS. However, Triton X-405 and the mixture of Span 80 and Tween 80 are not suitable, although their HLB values are in the acceptable range for emulsion polymerizations. DOSS, which works well in the polymerization of acrylates [49], is not suitable for the emulsion polymerization of IA esters. Although it is a sulfate, comparable with SDS, the emulsion polymerization yields are only about 5%.

The obtained molar masses do not differ significantly between the different reactions. In general, molar mass (M_n) of DEI as IA diester is lower compared to DBI. Based on the results, VA-044 and SDS are still the most promising combination and were utilized for the subsequent emulsion polymerizations.

Since the emulsions with VA-044 and the standard amount of SDS were not stable during long-time storage (agglomeration was observed), the amount of emulsifier was also doubled. This step slightly decreased the gravimetrically determined yield (25% for **P20** vs. 44% for **P5** and 75% for **P21** vs. 69% for **P11**). The results are summarized in Table 4.

2.3 | Comonomers

In addition to the already tested initiators and the emulsifiers, the choice of the (co)monomers also has an influence on the polymerization as already been seen for the investigations above. In general, the yield of the polymerization with DBI is higher than the yield with DEI (Figure 5; Table 5). Furthermore, the molar masses of the polymers with DBI are slightly higher than those of the polymers with DEI.

To understand this behavior, the water solubility of both monomers was determined and a low water solubility was detected: DEI 48 mmol $\mathrm{L^{-1}}$ and DBI below 4 mmol $\mathrm{L^{-1}}$. The water solubility of DBI is comparable to that of styrene (4.3 mmol $\mathrm{L^{-1}}$) [37].

The utilized monoester MBI has a water solubility of 32 mmol $\mathrm{L^{-1}}$.

Besides the already studied systems, other monoalkyl itaconates have also been considered. However, the shorter alkyl chains, such as monoethyl itaconate (MEI), are not suitable due to the higher water solubility of these monoesters (solubility of MEI in water: 1050 mmol $\mathrm{L^{-1}}$). The application of longer alkyl chains,

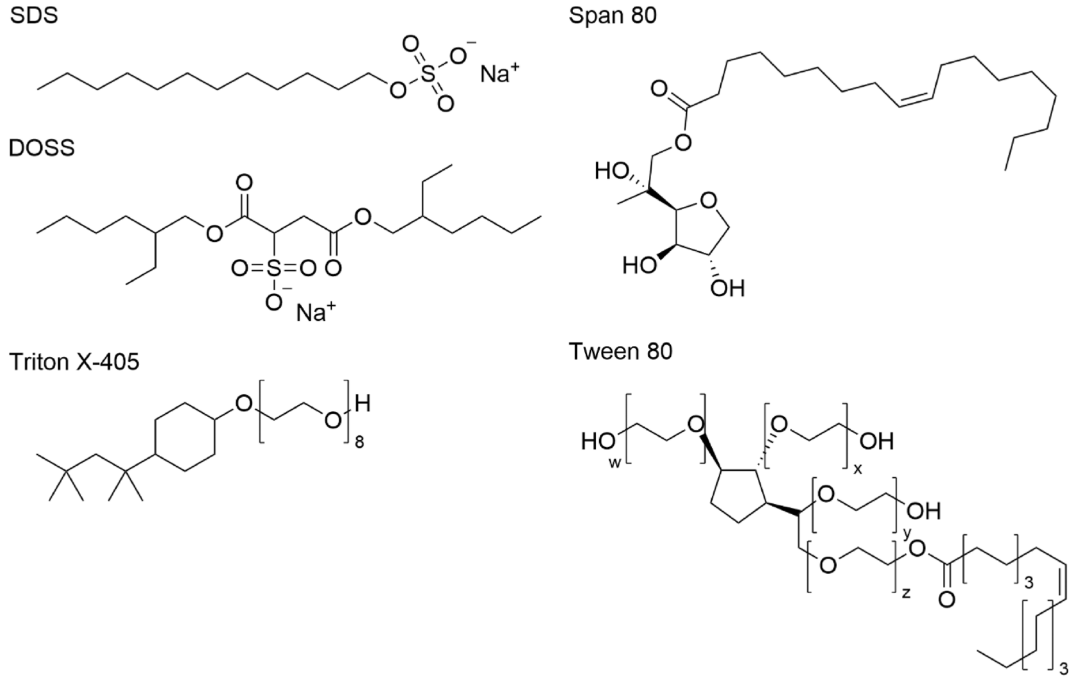


FIGURE 3 | Schematic representation of the emulsifiers utilized for the emulsion polymerization of itaconates.

TABLE 3 | Composition and analytical results of **P14**–**P19**.

			Initiator		Emulsifier					
Polymerization	**Diester type**	**Monoester type**	**[mmol]**	**Type**	**[g]**	**Type**	**M_n [g mol^{-1}]**[a]	**M_w [g mol^{-1}]**[a]	**$Đ$**[a]	**Yield [%]**
P14	DEI	MBI	0.225	VA-044	0.5	DOSS	14,100	53,200	3.78	5.3
P15	DBI	MBI	0.225	VA-044	0.5	DOSS	33,200	57,800	1.74	4.1
P16	DEI	MBI	0.225	VA-044	0.5	Triton X-405	34,000	84,300	1.51	21.1
P17	DBI	MBI	0.225	VA-044	0.5	Triton X-405	44,900	110,400	2.45	18.1
P18	DEI	MBI	0.225	VA-044	0.5	Span 80:Tween 80 (91:1)	6500	21,400	3.31	13.5
P19	DBI	MBI	0.225	VA-044	0.5	Span 80:Tween 80 (91:1)	5200	20,000	3.86	2.9

[a] Determined via SEC measurements (THF, PMMA-standard).

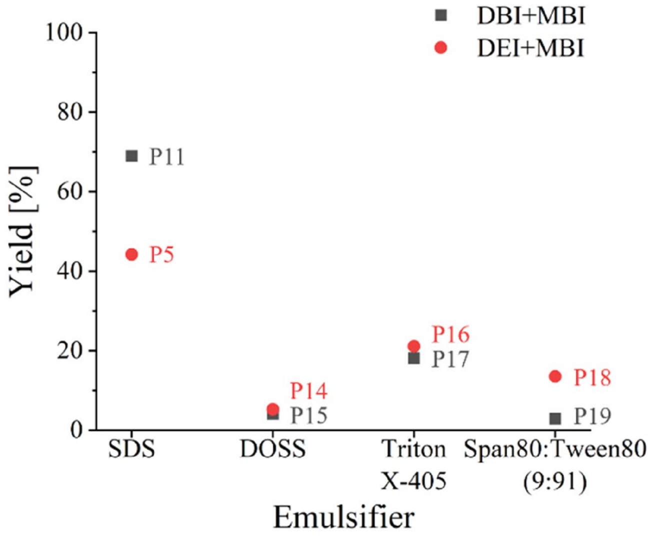


FIGURE 4 | Overview of the obtained yields of the emulsion polymerization using DBI and MBI (black) as well as DEI and MBI (red) with different emulsifiers. The composition of the emulsions is described in detail in Table 3.

like the MDI, has a solubility below 3 mmol L^{-1}, which was investigated.

In addition, the polymerization without the addition of a monoester was tested and these emulsions led to the highest yields (Figure 5).

The trend of lower yields when using monoesters is also evident for the molar mass. For DEI, M_n decreases from 33,000 g mol^{-1} (without monoester, **P24**) *via* 23,200 g mol^{-1} (with MBI, **P5**) to 17,000 g mol^{-1}(with MDI, **P26**). This trend is even more pronounced for DBI. Without monoester, M_n is 41,700 g mol^{-1} (**P25**), with MBI 32,500 g mol^{-1} (**P11**), and with MDI only 5800 g mol^{-1} (**P27**). Consequently, the choice of the itaconate, as well as the monoester, significantly influences the output of the emulsion polymerization.

2.4 | Influence of Concentration

Finally, the amount of water was varied to determine the influence of the concentration. The results are shown in Table 6. In this context, only slight variations regarding molar mass and yield could be observed. It can be seen that the yield is highest for **P28**. The amount of initiator, emulsifier and water was doubled compared to before. For **P29**, the quantity was increased by a factor of 1.5. For **P29**, the amount of emulsifier and water was increased by a factor of 1.5, but the amount of initiator was kept the same. The polymerization with the lowest monomer concentration (**P28**), therefore, has the highest yield. However, if Table 7 is also considered, it can be seen that the residual monomer content is higher than for **P29** and **P30**. This is presumably due to the fact that the dilution of the reaction solution results in fewer chain termination reactions, and therefore, the proportion of oligomers is lower.

Furthermore, the reproducibility of the emulsion process for itaconates was investigated and **P21** and **P23** were subsequently synthesized a second time and SEC measurements were

TABLE 4 | Composition and analytical results of **P20–P23**.

Polymerization	Diester type	Monoester type	Initiator [mmol]	Initiator Type	Emulsifier [g]	Emulsifier Type	M_n [g mol^{-1}][a]	M_w [g mol^{-1}][a]	$Đ$[a]	Yield [%]
P20	DEI	MBI	0.255	VA-044	0.125	SDS	24,800	50,400	2.03	7.1
P21	DEI	MBI	0.225	VA-044	1	SDS	8761	18,560	2.12	25.1
P22	DBI	MBI	0.255	VA-044	0.125	SDS	23,300	66,900	2.81	9.5
P23	DBI	MBI	0.225	VA-044	1	SDS	21,100	110,300	5.20	75.7

[a] Determined via SEC measurements (THF, PMMA-standard).

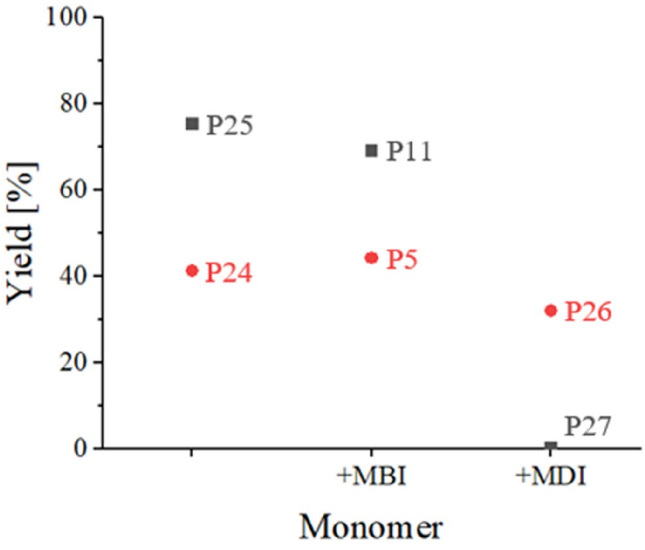


FIGURE 5 | Overview of the obtained yields of the emulsion with different itaconates (DEI—red, DBI—black).

performed (Table S3). These values differ only slightly from the previously determined ones showing the reliability of the synthetic pathway.

2.5 | Residual Monomer

For selected emulsions with high yields, the residual monomer content was also determined by gas chromatography–mass spectrometry (GC–MS) by performing the reaction a second time (Table 7). A defined amount of dodecane was added to the emulsion and the monomer content was determined based on this standard to provide information about the conversion of the monomers during the polymerization and not only about the gravimetrically obtained yield after dialysis. All of the measured emulsions had a very low residual monomer content, between 0.3% and 2.4%, showing the high benefit of emulsion polymerization, since the hardly polymerizable monomers, itaconates, can be efficiently converted to polymers. The emulsion with only DBI as monomer (**P25**) had the highest residual monomer content and the emulsion with DEI and MBI, with a doubled amount of SDS (**P21**) featured the lowest monomer content.

The difference between the determined yield and the residual monomer content is due to the fact that the lower molar masses of the oligomers are not recorded during dialysis and subsequent gravimetric determination.

2.6 | Particle Size

In addition, the particle size for selected emulsions was determined *via* DLS measurements (Table 8). These are the same emulsions in which the residual monomer content has already been determined and, therefore, have a high yield and are long-term stable. The results are shown in Table 8. The exact measurement results are shown in Table S12 and Figures S65–S71. In general, the particle size is between 40 and 200 nm, which is expected for an emulsion polymerization [37]. For polymers **P23** and **P28–P30**, different amounts of emulsifier were used, and it can be seen that they do not influence particle size significantly. **P25**, which is the polymer with no acid content, forms significantly smaller particles than comparable polymer with 5% acid content (**P11**).

The particle size was utilized to determine the concentration of the particles in the solution (for calculation, see Supporting Information; values are listed in Table 8). As can be seen, only **P11** has a lower concentration, as the particles are slightly larger than those of the other polymers. Together with **P25**, **P11** has the lowest emulsifier concentration, resulting in the largest particles for **P11**. The behavior of **P25** is different, and values comparable to those of other polymerizations can be found. **P25** is the homopolymer of DBI, whereas **P11** is the copolymer of DBI and MBI, which introduces additional charges from the monomer mixture.

3 | Conclusion

In summary, we have shown that the emulsion polymerization of IA esters, which are typically hard polymerizable monomers, reaching high conversions and molar masses is possible. Although $K_2S_2O_8$ is widely used in emulsion polymerization of styrene, it is not suitable for the emulsion polymerization of IA esters, as the free acid group of IA leads to accelerated decomposition. Azoinitiators, like the water-soluble VA-044, are a better choice as an initiator for the polymerization, in particular, in combination with SDS as an emulsifier. Other anionic and nonionic emulsifiers, which were tested as well, resulted in significantly lower yields of the polyitaconates. The nature of the utilized itaconate also strongly influenced the obtainable yields. MBI, in combination with DEI or DBI, resulted in the highest yields of up to 81% (after purification). GC measurements revealed that the residual monomer content was less than 1.3% for both the emulsions, that is, with DEI and with DBI, indicating a very high conversion of these bio-based monomers.

TABLE 5 | Composition and analytical results of **P24–P27**.

Polymerization	Diester type	Monoester type	Initiator		Emulsifier		M_n [g mol^{-1}][a]	M_w [g mol^{-1}][a]	$Đ$[a]	Yield [%]
			[mmol]	Type	[g]	Type				
P24	DEI		0.225	VA-044	0.5	SDS	33,000	372,800	11.30	41.27
P25	DBI		0.225	VA-044	0.5	SDS	41,700	95,400	2.30	75.2
P26	DEI	MDI	0.225	VA-044	0.5	SDS	17,000	56,800	3.30	32.0
P27	DBI	MDI	0.225	VA-044	1	SDS	5800	49,000	8.50	0.2

[a]Determined via SEC measurements (THF, PMMA-standard).

The herein presented emulsion polymerization of IA esters can open up the pathway to large-scale synthesis of bio-based polymers. This process has been available for the commercial oil-based acrylates and methacrylates and now also for their bio-based analogs, the itaconates.

4 | Experimental Section

4.1 | Materials

Sodium dihydrogen phosphate (NaH_2PO_4, Fluka), MBI (Sigma-Aldrich), DBI (Sigma-Aldrich), and itaconic anhydride (TCI) were used as received. DEI (TCI, stabilized with TBC) was purified over a column with neutral alumina (Molekula). MDI was synthesized using 1-dodecanol (TCI) and IA anhydride (TCI) analog to literature [56]. The initiators potassium persulfate ($K_2S_2O_8$, Fluka), ACPA (Sigma-Aldrich), VA-044 (TCI), V-50 (Sigma-Aldrich) and the emulsifiers SDS (TCI), Triton X-405 (Sigma-Aldrich), DOSS (Sigma-Aldrich), Span 80 (Sigma-Aldrich), and Tween 80 (Sigma-Aldrich) were used without further purification. Dialysis tubes (molecular weight cut-off: 1 kDa) were purchased from Carl Roth.

4.2 | Instrumentation

4.2.1 | Size-exclusion chromatography

SEC was performed on a Shimadzu 10er series equipped with a DGU-14A degasser, a CBM-20A controller, an LC-10AD vp pump, a SIL-10AD vp autosampler and a CTO-10A vp oven, a PSS SDV guard/linear M column with 5 μm particle size and a separation range of 400–1,000,000 g mol^{-1}. The flow rate was 1 mL min^{-1} at 30°C with tetrahydrofuran (THF) as eluent and PMMA as standard. As a refractive index detector (RID), a RID-10A and a UV detector (UVD), an SPD-10AD VP was used. The measurements were carried out in blocks of four to eight samples, with the device being calibrated before each measurement block.

One-dimensional nuclear magnetic resonance spectra (^1H) were recorded using a Bruker (Rheinstetten, Germany) AC 300 (300 MHz) at 298 K. ^{13}C spectra were recorded using an Avance NEO 500 (500.18 MHz, ^1H; 125.7 MHz, ^{13}C).

Elemental analysis was performed using a Vario El III (Elementar, Langensebold, Germany) elemental analyzer.

Dynamic light scattering (DLS) was performed for selected samples with a DynaPro Plate Reader III (Wyatt Technology Corporation, Santa Barbara, CA, USA). The laser has a wavelength of $\lambda = 820.9$ nm. Intensity fluctuations of the backscattered light were recorded at an angle of 150°. These were used for hydrodynamic size estimations based on the Stokes–Einstein equation. For each sample, five consecutive measurements (3 s acquisition time each) were performed at a temperature of 25°C. DLS data was processed with the Dynamics 7 software (Wyatt Technology Corporation, Santa Barbara, CA, USA). For the sample preparation, 5 μL of the emulsion was mixed with 520 μL of water.

4.3 | Gas Chromatography–Mass Spectrometry

4.3.1 | Analysis of the monomer

Five hundred microliters of the emulsion was mixed with 500 μL ethyl acetate. The mixture was briefly vortexed and centrifuged at 10,000 × g for 10 min. One microliter of the centrifugate was diluted with 89 μL ethyl acetate, combined with 10 μL of a dodecane standard solution (1 mg mL^{-1} dodecane in ethyl acetate) and subjected to GC–MS analysis.

For quantification, a calibration curve using dodecane as internal standard (10 μg mL^{-1} final concentration) and DBI in a concentration range from 10 to 100 μg mL^{-1} in 10 μg mL^{-1} steps as triplicates. Data integration was carried out using Thermo Xcalibur Quan Browser version 4.5.445.18. Retention time of dodecane was set to 11.04 and 16.26 min for DBI, respectively. Quantification ions were *m*/*z* 57.1 for dodecane and 113.0 for DBI, respectively. General settings for peak detection are: Mass deviation ±0.5 u; ICIS peak detection, smoothing points: 1, baseline window: 40, area noise factor: 5; peak noise factor: 10. Linear regression was performed with OriginPro 9.8.0.200. Calculations have been executed using Microsoft Excel Version 2010.

Samples were measured on a GC–MS system from Thermo Fisher Scientific GmbH (Bremen, Germany) consisting of a TRACE 1300 GC with an S/SL injector installed and an ITQ 900 ion trap mass spectrometer. The scan range was set between 45 and 550 *m*/*z*. The transfer line temperature was set to 300°C, the ion source temperature was set to 200°C, and the damping gas flow was set to 0.3 mL min^{-1} helium. Three micro scans were recorded at a maximum ion time of 25 ms. The filament delay was set to 5 min for the GC run time. After an initial 2 min at 40°C, the GC oven temperature was raised

TABLE 6 | Composition and analytical results of **P28–P30**.

Polymerization	Diester type	Monoester type	Initiator [mmol]	Initiator Type	Emulsifier [g]	Emulsifier Type	Water [mL]	M_n [g mol^{-1}][a]	M_w [g mol^{-1}][a]	$Đ$[a]	Yield [%]
P28	DBI	MBI	0.55	VA-044	1	SDS	100	17,000	80,300	4.70	80.9
P29	DBI	MBI	0.338	VA-044	0.75	SDS	75	21,700	74,700	3.44	61.2
P30	DBI	MBI	0.225	VA-044	0.75	SDS	75	17,600	107,400	6.10	72.4

[a] Determined via SEC measurements (THF, PMMA-standard).

to 320°C with 10°C min^{-1}. The injector was operated in split mode at 220°C with a flow rate of 10 mL min^{-1}, the split flow was 10, and the column flow was 1 mL min^{-1}. As column, a trace TR-5 ms SQC 30 m from Thermo Fisher Scientific GmbH was used, with 0.25 mm inner diameter and 0.25 µm film thickness. The autosampler AS200SE (CTC Analytics AG, Zwingen, Switzerland) injected 1 µL sample solution using the hot needle injection technique.

4.3.2 | Determination of Water Solubility

To determine the solubility of the monomers in water, the monomer was weighed out and mixed with 1 mL of water.

TABLE 7 | Residual monomer content of the emulsions determined *via* GC–MS measurements.

Polymerization	Residual monomer content [%]	Yield[a]
P11	0.9	69.0
P21	0.3	25.1
P23	1.3	75.7
P25	2.4	75.2
P28	1.0	80.9
P29	1.1	61.2
P30	0.5	72.4

[a] The yield was determined by the mass of the polymer after dialysis (1 kDa).

TABLE 8 | Particle size of the emulsion polymerization determined *via* DLS measurements.

Polymerization	Particle size [nm][a]	Particle concentration [10^{15} L^{-1}][a]
P11	195.8	89
P21	75.6	1629
P23	45.7	4227
P25	56.4	3602
P28	42.8	5146
P29	49.7	4108
P30	49.2	4235

[a] Particle size was determined *via* DLS measurements. The complete results can be found in Tables S6–S12.

TABLE 9 | Elemental analysis of MDI.

Element	Theoretical amount [%]	Measured amount [%]
C	68.42	68.40
H	10.13	10.12

TABLE 10 | Summary of the varied parameters for the different emulsion polymerizations (for details, see Table S1).

Polymerization	Diester [eq]	Type	Monoester [eq]	Type	Initiator [mmol]	Type	Emulsifier [g]	Type	NaH_2PO_4 [mg]	Water [mL]
P1	0.95	DEI	0.05	MBI	0.225	$K_2S_2O_8$	0.5	SDS	25	50
P2	0.95	DEI	0.05	MBI	0.45	$K_2S_2O_8$	0.5	SDS	25	50
P3	0.95	DEI	0.05	MBI	0.225	ACPA	0.5	SDS	25	50
P4	0.95	DEI	0.05	MBI	0.45	ACPA	0.5	SDS	25	50
P5	0.95	DEI	0.05	MBI	0.225	VA-044	0.5	SDS	25	50
P6	0.95	DEI	0.05	MBI	0. 45	VA-044	0.5	SDS	25	50
P7	0.95	DEI	0.05	MBI	0.255	VA-50	0.5	SDS	25	50
P8	0.95	DEI	0.05	MBI	0.45	VA-50	0.5	SDS	25	50
P9	0.95	DBI	0.05	MBI	0.45	$K_2S_2O_8$	0.5	SDS	25	50
P10	0.95	DBI	0.05	MBI	0.45	ACPA	0.5	SDS	25	50
P11	0.95	DBI	0.05	MBI	0.255	VA-044	0.5	SDS	25	50
P12	0.95	DBI	0.05	MBI	0.255	VA-50	0.5	SDS	25	50
P13	0.95	DBI	0.05	MBI	0.45	VA-50	0.5	SDS	25	50
P14	0.95	DEI	0.05	MBI	0.255	VA-044	0.5	DOSS	25	50
P15	0.95	DBI	0.05	MBI	0.255	VA-044	0.5	DOSS	25	50
P16	0.95	DEI	0.05	MBI	0.255	VA-044	0.5	Triton X-405	25	50
P17	0.95	DBI	0.05	MBI	0.255	VA-044	0.5	Triton X-405	25	50
P18	0.95	DEI	0.05	MBI	0.255	VA-044	0.5	Span 80:Tween 80 (91:1)	25	50
P19	0.95	DBI	0.05	MBI	0.255	VA-044	0.5	Span 80:Tween 80 (91:1)	25	50
P20	0.95	DEI	0.05	MBI	0.255	VA-044	0.0125	SDS	25	50
P21	0.95	DEI	0.05	MBI	0.255	VA-044	1	SDS	25	50
P22	0.95	DBI	0.05	MBI	0.255	VA-044	0.0125	SDS	25	50
P23	0.95	DBI	0.05	MBI	0.255	VA-044	1	SDS	25	50
P24	1	DEI	—		0.255	VA-044	0.5	SDS	25	50

(Continues)

TABLE 10 | (Continued)

Polymerization	Diester [eq]	Type	Monoester [eq]	Type	Initiator [mmol]	Type	Emulsifier [g]	Type	NaH_2PO_4 [mg]	Water [mL]
P25	1	DBI	—		0.255	VA-044	0.5	SDS	25	50
P26	0.95	DEI	0.05	MDI	0.255	VA-044	0.5	SDS	25	50
P27	0.95	DBI	0.05	MDI	0.255	VA-044	0.5	SDS	25	50
P28	0.95	DBI	0.05	MBI	0.45	VA-044	1	SDS	50	100
P29	0.95	DBI	0.05	MBI	0.3375	VA-044	0.75	SDS	37.5	75
P30	0.95	DBI	0.05	MBI	0.255	VA-044	0.75	SDS	37.5	75

After 24 h, it was checked whether it was dissolved in water. Different amounts of monomer were weighed in to determine the solubility.

4.4 | Synthesis of Monododecyl Itaconate

1-Dodecanol (9.317 g, 50 mmol) was placed in a 50 mL flask and heated to 110°C [56]. After the alcohol was melted, itaconic anhydride (5.605 g, 50 mmol) was added. The reaction was stirred at 110°C for 90 min. After the reaction solution was cooled, 25 mL of heptane was added. The obtained precipitate was transferred from the flask to a mortar and crushed. Subsequently, the powder was transferred back to the flask and stirred in 25 mL heptane for 4 h. The white residue was obtained by filtration and was dried.

^{1}H NMR (300 MHz, DMSO) $\delta = 0.84$ (m, 3H, CH_3 dodecyl), 1.23 (m, 18H, CH_2 dodecyl), 1.52 (m, 2H, CH_2 dodecyl), 2.49 (m, 4H, DMSO), 3.28–3.32 (d, 3H, CH_2 itaconic acid), 3.98 (t, 2H, CH_2 dodecyl), 5.74 and 6.13 (s, CH_2 itaconic acid double bond) ppm. Furthermore, elemental analyses of MDI were performed (Table 9).

4.5 | Synthesis of the Polymers

In a 150 mL sulfonation flask with stirrer shaft water, NaH_2PO_4 as a buffer, initiator and emulsifier were dissolved. The solution was degassed for 1 h, and then a solution of 25 mL monomer was added under stirring. Subsequently, the resulting solution was stirred at 60°C for 6 h. Then, the yield of the polymerization was determined gravimetrically. Therefore, the emulsion was purified *via* dialysis (molecular weight cut-off: 1 kDa) for 3 days in water and 8 days in THF. Meanwhile, the solvent was changed once every day. Furthermore, the emulsions with a yield above 60% were analyzed *via* GC–MS regarding the residual monomer content by performing the corresponding reaction a second time. In Table 10, the different polymerization conditions are summarized.

Our cooperation partner carried out the syntheses of **P21** and **P23** several times and determined the molar masses using SEC. The results are shown in Table S3.

Acknowledgments

The authors would like to thank the Bundesministerium für Ernährung und Landwirtschaft (BMEL) *via* the Fachagentur Nachwachsende Rohstoffe (FNR) for funding (funding number: 2220NR070A and 2220NR070B).

References

1. S. Molina-Gutierrez, V. Ladmiral, R. Bongiovanni, S. Caillol, and P. Lacroix-Desmazes, “Radical Polymerization of Biobased Monomers in Aqueous Dispersed Media,” *Green Chemistry* 21, no. 1 (2019): 36–53, https://doi.org/10.1039/C8GC02277A.

2. R. M. Cywar, N. A. Rorrer, C. B. Hoyt, G. T. Beckham, and E. Y.-X. Chen, “Bio-Based Polymers With Performance-Advantaged Properties,”

Nature Reviews Materials 7, no. 2 (2022): 83–103, https://doi.org/10.1038/s41578-021-00363-3.

3. C. R. Casas-Soto, A. S. Conejo-Davila, V. Osuna, et al., "Dibutyl Itaconate and Lauryl Methacrylate Copolymers by Emulsion Polymerization for Development of Sustainable Pressure-Sensitive Adhesives," *Polymers* 14, no. 3 (2022): 632, https://doi.org/10.3390/polym14030632.

4. D. K. Schneiderman and M. A. Hillmyer, "50th Anniversary Perspective: There Is a Great Future in Sustainable Polymers," *Macromolecules* 50, no. 10 (2017): 3733–3749, https://doi.org/10.1021/acs.macromol.7b00293.

5. S. Kobayashi, "Green Polymer Chemistry: New Methods of Polymer Synthesis Using Renewable Starting Materials," *Structural Chemistry* 28, no. 2 (2017): 461–474, https://doi.org/10.1007/s11224-016-0861-3.

6. F. L. Hatton, "Recent Advances in RAFT Polymerization of Monomers Derived From Renewable Resources," *Polymer Chemistry* 11, no. 2 (2020): 220–229, https://doi.org/10.1039/C9PY01128E.

7. K. Yahiro, T. Takahama, Y. S. Park, and M. Okabe, "Breeding of *Aspergillus terreus* Mutant TN-484 for Itaconic Acid Production With High Yield," *Journal of Fermentation and Bioengineering* 79, no. 5 (1995): 506–508, https://doi.org/10.1016/0922-338x(95)91272-7.

8. M. Okabe, D. Lies, S. Kanamasa, and E. Y. Park, "Biotechnological Production of Itaconic Acid and Its Biosynthesis in *Aspergillus terreus*," *Applied Microbiology and Biotechnology* 84, no. 4 (2009): 597–606, https://doi.org/10.1007/s00253-009-2132-3.

9. W. E. Levinson, C. P. Kurtzman, and T. M. Kuo, "Production of Itaconic Acid by *Pseudozyma antarctica* NRRL Y-7808 Under Nitrogen-Limited Growth Conditions," *Enzyme and Microbial Technology* 39, no. 4 (2006): 824–827, https://doi.org/10.1016/j.enzmictec.2006.01.005.

10. J. Becker, H. Hosseinpour Tehrani, M. Gauert, J. Mampel, L. M. Blank, and N. Wierckx, "An *Ustilago maydis* Chassis for Itaconic Acid Production Without By-Products," *Microbial Biotechnology* 13, no. 2 (2020): 350–362, https://doi.org/10.1111/1751-7915.13525.

11. A. Li, N. Pfelzer, R. Zuijderwijk, A. Brickwedde, C. Zeijl, and P. Punt, "Reduced By-Product Formation and Modified Oxygen Availability Improve Itaconic Acid Production in *Aspergillus niger*," *Applied Microbiology and Biotechnology* 97, no. 9 (2013): 3901, https://doi.org/10.1007/s00253-012-4684-x.

12. H. Hajian and W. M. Wan Yusoff, "Itaconic Acid Production by Microorganisms: A Review," *Current Research Journal of Biological Sciences* 7, no. 2 (2015): 37–42, https://doi.org/10.19026/crjbs.7.5205.

13. T. Robert and S. Friebel, "Itaconic Acid—A Versatile Building Block for Renewable Polyesters With Enhanced Functionality," *Green Chemistry* 18, no. 10 (2016): 2922, https://doi.org/10.1039/c6gc00605a.

14. S. Brännström, E. Malmström, and M. Johansson, "Biobased UV-Curable Coatings Based on Itaconic Acid," *Journal of Coating Technology and Research* 14, no. 4 (2017): 851–861, https://doi.org/10.1007/s11998-017-9949-y.

15. M. Winkler, T. M. Lacerda, F. Mack, and M. A. R. Meier, "Renewable Polymers from Itaconic Acid by Polycondensation and Ring-Opening-Metathesis Polymerization," *Macromolecules* 48, no. 5 (2015): 1398–1403, https://doi.org/10.1021/acs.macromol.5b00052.

16. C. Kozbekci, B. F. Senkal, and C. Erbil, "Compressive Moduli and Network Parameters of *N*-Isopropylacrylamide Hydrogels Copolymerized by Monoesters of Itaconic Acid and Crosslinked With Tetraallylammonium Bromide," *Journal of Applied Polymer Science* 134, no. 29 (2017): 45039, https://doi.org/10.1002/app.45039.

17. M. Yu, H. Chen, Y. Liang, et al., "Porous Acrylonitrile/Itaconic Acid Copolymers Prepared by Suspended Emulsion Polymerization," *Journal of Applied Polymer Science* 111, no. 6 (2009): 2761–2768, https://doi.org/10.1002/app.29339.

18. C. S. Marvel, "Polymerization Reactions of Itaconic Acid and Some of Its Derivatives," *Journal of Organic Chemistry* 24 (1959): 599–605, https://doi.org/10.1021/jo01087a006.

19. A. M. Lehman-Chong, C. L. Cox, E. Kinaci, et al., "Itaconic Acid as a Comonomer in Betulin-Based Thermosets via Sequential and Bulk Preparation," *ACS Sustainable Chemistry & Engineering* 11 (2023): 14216–14225, https://doi.org/10.1021/acssuschemeng.3c04178.

20. J. Gupta, R. Tomovska, and M. Aguirre, "Overcoming Challenges of Incorporation of Biobased Dibutyl Itaconate in (Meth)Acrylic Waterborne Polymers," *Biomacromolecules* 25, no. 8 (2024): 5310–5320, https://doi.org/10.1021/acs.biomac.4c00739.

21. D. Shi, Y. Gao, L. Sun, and M. Chen, "Superabsorbent Poly(Acrylamide-Co-Itaconic Acid) Hydrogel Microspheres: Preparation, Characterization and Absorbency," *Polymer Science* 56, no. 3 (2014): 275–282, https://doi.org/10.1134/S0965545X14030146.

22. A. Gordon and K. Coupland, "Germany Mehrzweckschmiermittel. DE3001000," 1970.

23. J. E. Smith, A. Nowakowska-Waszczuk, and J. G. Anderson, "Organic Acid Production by Mycelial Fungi," in *Industrial Aspects of Biochemistry, Part A*, ed. B. Spencer (Amsterdam: Federation of European Biochemical Societies, 1974).

24. Z. Hua and X. Fang, "Robust Itaconic Acid-Based Polymer Adhesive Nanocomposites Containing Bioinspired Multiple Hydrogen Bonds at the Polymer–Nanofiller Interface," *Macromolecules* 56 (2023): 8047–8053, https://doi.org/10.1021/acs.macromol.3c01395.

25. D. Braun and I. A. A. El Sayed, "Über die struktur der polymeren aus itaconsäure," *Macromolecular Chemistry and Physics* 96 (1966): 100–121, https://doi.org/10.1002/macp.1966.020960108.

26. D. Stawski and S. Polowinski, "Polymerization of Itaconic Acid," *Polimery* 50, no. 2 (2005): 118–122.

27. J. Herrera-Ordonez, "New Insights on the Kinetics of Persulfate-Initiated Itaconic Acid Free-Radical Polymerization," *Macromolecular Reaction Engineering* 17 (2023): 2300022, https://doi.org/10.1002/mren.202300022.

28. L. Sollka and K. Lienkamp, "Progress in the Free and Controlled Radical Homo- and Co-Polymerization of Itaconic Acid Derivatives: Toward Functional Polymers with Controlled Molar Mass Distribution and Architecture," *Macromolecular Rapid Communications* 42, no. 4 (2021): 2000546, https://doi.org/10.1002/marc.202000546.

29. D. Malferrari, N. Armenise, S. Decesari, P. Galletti, and E. Tagliavini, "Surfactants from Itaconic Acid: Physicochemical Properties and Assessment of the Synthetic Strategies," *ACS Sustainable Chemistry & Engineering* 3, no. 7 (2015): 1579–1588, https://doi.org/10.1021/acssuschemeng.5b00264.

30. S. Bednarz, S. Bujok, K. Mielczarek, et al., "Synthesis of Low-Molecular Weight Itaconic Acid Polymers as Nanoclay Dispersants and Dispersion Stabilizers," *Polymer* 265 (2023): 125614, https://doi.org/10.1016/j.polymer.2022.125614.

31. J. Meurer, J. Hniopek, J. Dahlke, et al., "Novel Biobased Self-Healing Ionomers Derived From Itaconic Acid Derivates," *Macromolecular Rapid Communications* 42, no. 8 (2021): 2170031, https://doi.org/10.1002/marc.202170031.

32. T. Hirano, S. Tateiwa, M. Seno, and T. Sato, "Temperature Dependence of Stereospecificity in the Radical Polymerization of Di-*N*-Butyl Itaconate in Bulk," *Journal of Polymer Science, Part A: Polymer Chemistry* 38, no. 13 (2000): 2487, https://doi.org/10.1002/1099-0518(20000701)38:13<2487::AID-POLA200>3.0.CO;2-L.

33. A. Y. Sankhe, S. M. Husson, and S. M. Kilbey, "Effect of Catalyst Deactivation on Polymerization of Electrolytes by Surface-Confined Atom Transfer Radical Polymerization in Aqueous Solutions," *Macromolecules* 39, no. 4 (2006): 1376–1383, https://doi.org/10.1021/ma0519361.

34. C. Deoghare, C. Baby, V. S. Nadkarni, R. N. Behera, and R. Chauhan, “Synthesis, Characterization, and Computational Study of Potential Itaconimide-Based Initiators for Atom Transfer Radical Polymerization,” *RSC Advances* 4, no. 89 (2014): 48163–48176, https://doi.org/10.1039/c4ra08981b.

35. K. Satoh, D.-H. Lee, K. Nagai, and M. Kamigaito, “Precision Synthesis of Bio-Based Acrylic Thermoplastic Elastomer by RAFT Polymerization of Itaconic Acid Derivatives,” *Macromolecular Rapid Communications* 35 (2014): 161–167, https://doi.org/10.1002/marc.201300638.

36. J. M. Asua, “Emulsion Polymerization: From Fundamental Mechanisms to Process Developments,” *Journal of Polymer Science, Part A: Polymer Chemistry* 42 (2003): 1025–1041, https://doi.org/10.1002/pola.11096.

37. P. A. Lovell and F. J. Schork, “Fundamentals of Emulsion Polymerization,” *Biomacromolecules* 21 (2020): 4396–4441, https://doi.org/10.1021/acs.biomac.0c00769.

38. Y. Durant, US 2011/0144265 Al, 2011.

39. J. M. G. Cowie and Z. Haq, “Poly(Alkyl Itaconates) Part V Copolymers of Selected Mono- and Di-Alkyl Esters,” *European Polymer Journal* 13 (1977): 745–750, https://doi.org/10.1016/0014-3057(77)90016-7.

40. S. Sugihara, Y. Kawamoto, and Y. Maeda, “Direct Radical Polymerization of Vinyl Ethers: Reversible Addition–Fragmentation Chain Transfer Polymerization of Hydroxy-Functional Vinyl Ethers,” *Macromolecules* 49, no. 5 (2016): 1563–1574, https://doi.org/10.1021/acs.macromol.6b00145.

41. Sigma-Aldrich, Applications: Free Radical Initiators; Thermal Initiators: Decomposition Rate and Half-Life, accessed December 8, 2024, https://www.sigmaaldrich.com/deepweb/assets/sigmaaldrich/marketing/global/documents/411/888/thermal_initiators.pdf.

42. FUJIFILM, Wako Chemicals Europe GmbH, V-50, accessed December 8, 2024, https://specchem-wako.fujifilm.com/europe/en/water-soluble-azo-initiators/V-50.htm.

43. D. Cochin, A. Laschewsky, and F. Nallet, “Emulsion Polymerization of Styrene Using Conventional, Polymerizable, and Polymeric Surfactants. A Comparative Study,” *Macromolecules* 30 (1997): 2278–2287, https://doi.org/10.1021/ma9614510.

44. T. Hirano, R. Takeyoshi, M. Seno, and T. Sato, “Chain-Transfer Reaction in the Radical Polymerization of Di-*N*-Butyl Itaconate at High Temperatures,” *Journal of Polymer Science, Part A: Polymer Chemistry* 40 (2002): 2415–2426, https://doi.org/10.1002/pola.10316.

45. T. Hirano, K. Higashi, M. Seno, and T. Sato, “Radical Polymerization of Di-*N*-Butyl Itaconate in the Presence of Lewis Acids,” *European Polymer Journal* 2003 (1801): 39–1808, https://doi.org/10.1016/S0014-3057(03)00105-8.

46. K. Tauer and R. Deckwer, “Polymer End Groups in Persulfate-Initiated Styrene Emulsion Polymerization,” *Acta Polymerica* 49, no. 8 (1998): 411–416, https://doi.org/10.1002/(sici)1521-4044(199808)49:8<411::aid-apol411>3.0.co;2-d.

47. M. R. Lock, M. S. El-Aasser, A. Klein, and J. W. Vanderhoff, “Investigation of the Persulfate/Itaconic Acid Interaction and Implications for Emulsion Polymerization,” *Journal of Applied Polymer Science* 39, no. 10 (1990): 2129–2140, https://doi.org/10.1002/app.1990.070391008.

48. T. F. Tadros, “Emulsion Formation, Stability, and Rheology,” in *Emulsion Formation and Stability*, ed. T. F. Tadros (Weinheim: Wiley-VCH, 2013), 1–75.

49. W. Breuer and R. Höfer, “Sulfosuccinates for Emulsion Polymerization,” *Tenside, Surfactants, Detergents* 40, no. 4 (2006): 208–214.

50. A. Gadhave, “Determination of Hydrophilic-Lipophilic Balance Value,” *International Journal of Science and Research* 3, no. 4 (2014): 573–575.

51. H.-D. Dörfler, *Grenzflächen- und Kolloidchemie* (Weinheim: VCH, 1994).

52. E. Slinde and T. Flatmark, “Effect of the Hydrophile-Lipophile Balance of Non-Ionic Detergents (Triton X-Series) on the Solubilization of Biological Membranes and Their Integral B-Type Cytochromes,” *Biochimica et Biophysica Acta, Biomembranes* 455 (1976): 796–805, https://doi.org/10.1016/0005-2736(76)90049-3.

53. D. Colombie, E. D. Sudol, and M. S. El-Aasser, “Role of Mixed Anionic−Nonionic Systems of Surfactants in the Emulsion Polymerization of Styrene: Effect on Particle Nucleation,” *Macromolecules* 33, no. 20 (2000): 7283–7291, https://doi.org/10.1021/ma9920588.

54. K. I. Suresh, J. Othegraven, K. V. S. N. Raju, and E. Bartsch, “Mechanistic Studies on Particle Nucleation in the Batch Emulsion Polymerisation of *N*-Butyl Acrylate Containing Multifunctional Monomers,” *Colloid & Polymer Science* 283, no. 1 (2004): 49–57, https://doi.org/10.1007/s00396-004-1088-1.

55. Society of Cosmetic Chemists, “A Time Saving Guide to Surfactant Selection. Chemaxon,” 2004, https://docs.chemaxon.com/display/docs/attachments/attachments_1831051_1_The_HLB_System.pdf.

56. J.-V. Richard, C. Delaite, G. Riess, and A.-S. Schuller, “A Comparative Study of the Thermal Properties of Homologous Series of Crystallisable *N*-Alkyl Maleate and Itaconate Monoesters,” *Thermochimica Acta* 623 (2016): 136–143, https://doi.org/10.1016/j.tca.2015.10.015.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.