

DEVELOPMENT OF DEPOSIT CONTROL ADDITIVES FOR DIESEL FUEL

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Abstract

During the research activity a new, raw material and energy-saving technology has been developed for the preparation of polyisobutylene(PIB)-succinimide type diesel fuel additives. PIB-succinic-anhydride type intermediers having new structure were obtained as the products of radical initiation-based synthesis. The intermediers were used to acylate polyethylene polyamines to produce the final product. The synthesised final products have shown better analytical and performance properties such as improved deposit control efficiency. In the second part of the paper, the incorporation of fatty acid methyl ester into the molecular structure of PIB-succinic-anhydride has been studied to widen the functions and enhance the performance of the succinimide type additive family. During the product-improvement the advantageous reaction parameters have been determined. It was concluded, that the synthesized fuel additives can dissolve in diesel fuel perfectly, had excellent corrosion inhibiting- and lubricity improving effects and the DD efficiency of traditional succinimides could be achieved moreover in some cases exceeded. Based on the IR, GPC, ¹³C and ¹H NMR analytical tests original molecular structures of both additive types were confirmed.

Keywords: Diesel fuel; fuel additives; polyisobutylene-succinic anhydride; synthesis with radical initiation; fatty acid methyl ester; PIB-succinimide; deposit control additives.

1. Introduction

Engine fuels are comprised of "green", high quality blending components and highly efficient additives. Nowadays, application of high performance additives is essential to meet the required fuel properties and to protect the engine and the environment [1, 2].

Out of the numerous additive types, Deposit Control Additives (DCAs) are applied in the highest amount. Deposits may form in the fuel injector system of the engine. These deposits influence the emission, fuel economy, cold start behaviour, driveability and performance, too. DCAs are generally long chain hydrocarbons attached to a polar head group. Deposit precursors are attracted to the deposit control molecule, and become bounded into the dispersant micelles. At normal operating temperatures the DCA is a liquid that forms a thin film on the surface of the inlet system. The thin film is driven forward by air and fuel vapour flow, but forms a first line barrier to deposit precursors as well as a dispersant/neutraliser of the precursors protecting the metal surface. In the case of deposits on the metal surface, the liquid film slowly removes them by a detergent action [1,2].

Diesel fuel detergents are predominantly based on ashless polymeric products. Among these polyisobutylene-based different alkene-, alkyl-, polyalkene-, polyalkyl-succinic anhydrides derivatives are applied in highest amount. The derivatives of succinic anhydrides are usually produced in two steps: the first step is the preparation of polyisobutylene-succinic anhydrid (PIBSA) by ene-reacton between polyisobutylene and maleic anhydride. In case of fuel detergents, the main reaction type are the thermally initiated and catalytic reactions. In the second step, the intermediates synthesized through the first step are used to acylate amines, amino alcohols, alcohols etc.

Possibilities for the next reactions and the properties of the final products significantly depend on the structure and purity of the resultant intermediate as well as the conversion of MA- and olefin. The main research ways targeting the improvement of the reaction parameters are the thermal or radical initiation, catalytic synthesis or their combinations^[3].

Fatty acid methyl esters (FAME) and/or their derivatives are able to substitute diesel fuels and/or their additives. The use of FAMEs can reduce the import dependence of crude oil and its products. The application of esters based on vegetable oils in premium quality diesel fuels ensures environmental advantages (lower CO₂-emission, biodegradability, non-toxic, etc.). Many vegetable oils can be used as a source of methyl ester production; however, the application of the rapeseed- and the sunflower-oils is the most wide-spread because their properties are the most similar to those of diesel fuel. Their advantage is the good lubricity and the smaller emission of particulate matter^[4]. A more and more significant utilization option of vegetable oils resulting in substantial value addition is the production of additives that are useful for various industrial purposes. This utilization option is not only motivated by their renewable nature and their superior biodegradability compared to synthetic products, but also by their applicability in various chemical reactions or structural modifications due to the unique distribution of their unsaturated bonds and their reactive functional groups^[5].

2. Experimental

The aim of our research work was the development of polyisobutylene-based, ash-free detergent dispersant additives of diesel fuel. Our main purpose was the elimination of the disadvantages of the thermic PIBSA-synthesis (high energy demand and reaction time, not too bright color etc.) and the demand of distinguishable product (new product-structure). Beside these, the other objective of our work was the development of a multifunctional fuel additive containing bio-component as molecular-constituent. With the incorporation of fatty acid methyl ester into the molecular structure we wished to widen the functions and enhance the performance (lubricity improving and corrosion inhibiting effect) of the succinic imide type additive family and also to increase its biodegradability.

2.1 Materials

For the synthesis of PIBSA commercially available polyisobutylenes (PIBs) were selected, their main properties are summarized in Table 1. Beside PIBs, maleic anhydride (MA, produced by MOL), aromatic solvent, and radical initiator and – in the second part of this research work – rapeseed oil methyl ester (RME, prepared by us), were used in the first step. Polyethylene polyamines and base oil (as solvent oil, SN-150) was applied for the preparation of final products.

Table 1 The main properties of polyisobutylenes

Properties	PIB	R-PIB	HR-PIB
Appearance	Clear and bright		
Molecular weight, \overline{M}_n	910	1030	1050
Polydispersity	1.60	1.82	1.52
α vinylidene content, %	<80	84.7	88
KV at 100°C, mm ² /s	223.6	190.0	192
Flashpoint (COC), °C	214	190	204
Iodine-bromine number, gI/100 g	47.8	49.1	35.6

PIB: polyisobutylene, R-PIB: reactive polyisobutylene, HR-PIB: highly reactive polyisobutylene

2.2 Experimental methods

The analytical and performance tests of the intermediates and the final products were carried out according to international and local standards and proprietary methods (Tab 2).

Table 2 Analytical and performance tests

Properties	Methods	Performance tests	Methods
Kinematic viscosity (KV)	EN ISO 3104	Potential DD Efficiency (PDDE)	proprietary (paper chromatography and centrifugation)
Total Base Number (TBN)	ISO 3771		
Nitrogen content	modified Kjeldahl		
Active material content	local standard (column chromatography)	Peugeot XUD-9A/L engine test	CEC F-23-A-00
Total Acid Number (TAN)	proprietary (titrimetric)	Lubricity	EN ISO 12156-1 ASTM D 4172
Saponification Number (SN)	ISO 6293		
Maleic anhydride content	proprietary (titrimetric)	Copper strip test	ISO 2160:2000
Molecular weight and its distribution	proprietary (GPC)	Steel drift test	ASTM D 665
Molecular structure	IR spectroscopy NMR spectroscopy		

2.3. Experimental design

The polyisobutylene-succinic anhydrides were prepared in a four-neck flask equipped with a stirrer, a reflux cooler, a thermometer and a raw-materials feeder. The reaction was carried out at atmospheric pressure and different temperatures (max 150°C) in aromatic solvent (< 30%), with radical initiation (<15%) and various molar ratios of the reactants (MA/PIB:1,0:1,0 – 1,0:2,0 and PIB/RME/MA – 1,0:0,8:0,8-1,0:1,3:1,4). The solvent and the unreacted materials were removed at 200 °C by vacuum distillation.

Selected intermediates were used to acylate polyethylene polyamines. The additives were prepared under inert N₂ atmosphere in a five-neck flask equipped with a stirrer, a reflux cooler, a thermometer and a N₂ feeder. Polyethylene polyamines were added to the intermediate containing base oil (SN-150) by continuous stirring. The acylating reactions were carried out at 165-185 °C under mild vacuum with a reaction time of 4-6 hours (according to well known methods in the synthesis of polyalkylene succinimides). Unreacted polyamines were removed at 200°C by vacuum distillation.

3. Results and Discussion

3.1. Production and laboratory investigation of the polyisobutylene-succinic anhydride derivatives prepared by radical initiation

The properties of some typical intermediate products, synthesised from different PIBs by thermally initiated (TI) and by radically initiated (RI) processes, are shown in Table 3. It can be seen that the synthesis of intermediate products from low reactivity PIB (α vinylidene content <80%) were carried out by low conversion and thus with low active material content. The coupling ratio was lower than it was expected at this molecular weight. To reach the 1:1 SA/PIB coupling ratio it was possible only at 2:1 MA/PIB feedstock molar ratio. A significantly higher conversion was achieved in case of the other two PIBs where the coupling ratios were also higher. There was a lower difference between the high reactivity (HR-PIB) and the reactive (R-PIB) PIBs. The conversions were about 80% in case of intermedier produced from R-PIB while it was ~90% in case of the PIBSA synthesised from HR-PIB.

From the additive production point of view the most advantageous reaction parameters and molar ratio of the components were determined by laboratory and pilot plant experiments. By applying accurate amount of components, temperature and reaction time intermediate products (polyisobutylene succinic anhydride = PIBSA) could be synthesized from PIB having $\bar{M}_n \sim 1000$. Using these parameters, intermedier products having different MA/PIB connection ratio can be produced.

It has been determined that in case of PIBDISA (MA-PIB molar ratio 2:1) production the reaction time of the second MA ring connecting to the PIB chain is much longer, therefore the longer time of the synthesis is preferred to produce this intermediate, meanwhile decreasing the unreacted MA results in less PIBDISA type molecules.

Table 3 Properties of some typical synthesized PIBSAs

Properties	PIBSA	R-PIBSA	HR-PIBSA	Commercial**
PIB	PIB	R-PIB	HR-PIB	HR-PIB
MA/PIB molar ratio	1.0	1.0	1.0	1.1
Type of process	RI	RI	RI	TI
Temperature, °C	max 150	max 150	max 150	above 210
Solvent	aromatic	aromatic	aromatic	-
Active material, % m/m	33.0		76.3	-
KV at 100°C, mm ² /s	819	822.3	891	80.0
TAN mg KOH/g	43.0	82.8	98.4	64.0
Conversion*, %	53.4	77.0	89.2	-
MA/PIB coupling ratio	0.5	0.82	0.96	-

* based on theoretical TAN; ** containing 50% base oil

By using IR, GPC, ¹³C and ¹H NMR techniques, the molecular structure of the PIBSAs were investigated. The results of the IR spectroscopy (Tab 4.) showed that the reaction between the MA and PIBs was carried out.

Based on the results of the ¹H and ¹³C NMR tests^[6] the difference of the molecular structure between the PIBSA produced by radically initiated method and thermal way has been determined. The PIBSA synthesised by thermal way mainly contains molecules having 1:1 PIB-SA connection ratio. The PIBSA produced by radical initiated method consist of – in addition of the above mentioned molecule – succinic anhydride substituted with two PIB molecules, which ensures the dispersant effect, and there are some polyisobutene molecules connected with two or more succinic anhydride rings, which can improve the detergent effect due to the formation of more polar molecules. Based on the structure investigation, some possible structures of the intermediate are demonstrated on Figure 1.

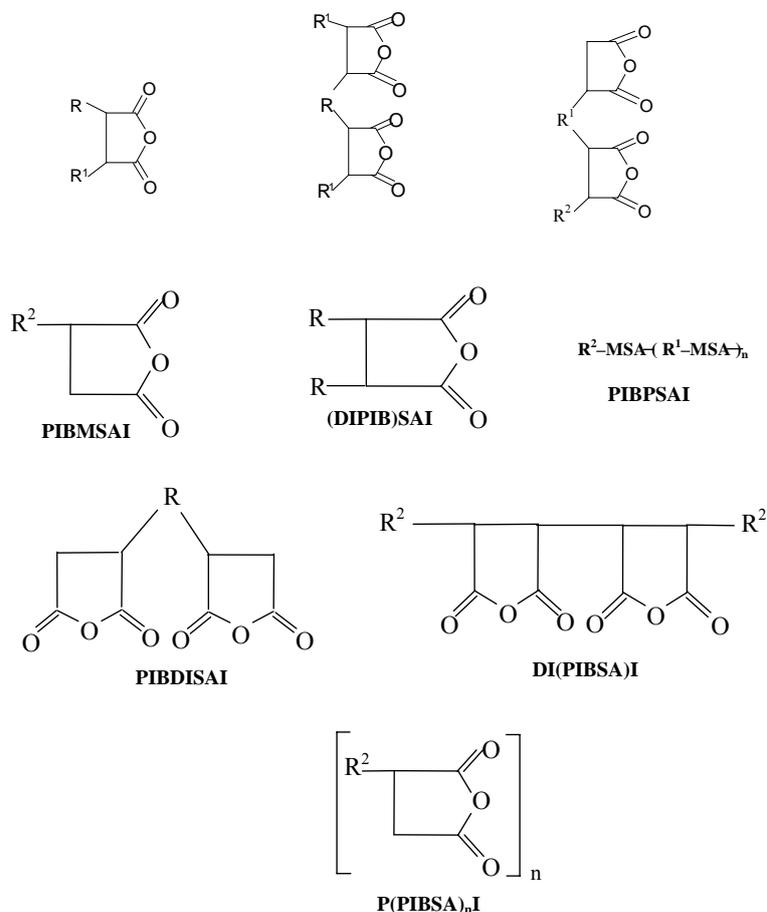
Table 4 Typical absorption maximums of PIBSAs and succinimides

Typical absorption maximums, cm ⁻¹	Vibration type	Chemical groups	Sample
1870-1700	ν C=O	Anhydrides with five carbon atoms	PIBSA
1770-1700	ν C=O	Imides	Succinimide
1080	ν_{sz} C-O(H)	Primer OH bonds	PIBSA
1485-1445	β_s CH ₂	Saturated bonds of polyisobutenes	PIBSA, Succinimide
750-700	β CH ₂	Saturated bonds of polyisobutenes	PIBSA, Succinimide
1395-1365	$\gamma\sigma$ CH ₃	Saturated bonds of polyisobutenes	PIBSA, Succinimide
3000-2800	$\beta\sigma$ CH ₂ , $\beta\alpha\sigma$ CH ₂	Saturated bonds of polyisobutenes	PIBSA, Succinimide
990-890	C=C	Olefinic bonds of polyisobutenes	PIBSA
990-890	C=C	Olefinic bonds of polyisobutenes	PIBSA
3300-3150	ν NH	Amide-V	PIBSA

There were mono-(PIBMSI) and bis-succinimides(PIBBSI) synthesized from the previously shown intermediate products, their properties are listed in Table 5. It was concluded, that the values of the TBN and nitrogen content changed according to the active material content of the intermediate products. The properties of the low reactivity PIBs were significantly lower than the usual values. Besides, their detergent-dispersant efficiencies

(PDDE) were relatively good. PDDE values of the succinimides synthesized from higher reactivity PIBs reached the level of the commercially available succinimides.

Based on IR analysis (Tab. 4), the formation of PIB-succinimides structure was determined.



R and *R*² = polyisobutylene group with 30-80 C-number; *R*¹ = alkyl group with 2-5 C-number;

PIBMSAI: PIB mono-succinic anhydride prepared by radical initiation

PIBDISAI: PIB di-succinic anhydride prepared by radical initiation

(DIPIB)SAI: (di-PIB) succinic anhydride prepared by radical initiation

DI(PIBSA)I: di-(PIB succinic anhydride) prepared by radical initiation

P(PIBSA)_nI: poly (PIB succinic anhydride) prepared by radical initiation

Figure 1 The possible structures of the intermediates

Table 5 Properties of some typical synthesized polyisobutylene succinimides (PIBSI)

Properties	PIBMSI	PIBBSI	R-PIBMSI	R-PIBBSI	HR-PIBMSI	HR-PIBBSI		
KV at 100°C, mm ² /s	172.1	159.5	92.8	90.4	150.3	115*	90.3	70*
Oil content, %	50	50	50	50	50	50	50	50
TBN, mg KOH/g	3.33	0.71	-	-	60.5	90	25.0	21.6
N-content, %	0.34	0.19	-	-	2.5	3.25	1.35	1.03
Detergent Index (DI), %	100	100	97	100	100	100	100	100
Washing efficiency (W), mm (max 125)	64	24	85	82	94	87	93	95
PDDE, % (max 100)	73	55	81	81	86	83	86	86

* commercial

Based on these results and the ^1H and ^{13}C NMR tests [9] it was found, that the fatty acid methyl ester can be built into the PIB-succinic anhydride structure, thus producing a novel compound having original structure.

The preferred intermediates were used to produce final product. The polyisobutylene-succinic anhydrides containing fatty acid methyl ester were diluted with base oil (SN-150) to reduce their viscosity, and different polyethylene polyamines (PEPA) were acylated with it at various PEPA/PIBSAF molar ratio. Main properties of some typical succinic derivatives (PIBFSI) were given in Tab 7.

The synthesized additives were dissolved in SN-150 base oil in 3% concentration for the DD efficiency tests. The detergent index of all products was 100%. The results of their washing effect and potential DD effect showed that efficiency of traditional succinics could be achieved (Tab 7.).

Based on the copper strip corrosion test, it was found, that the additives had excellent corrosion inhibiting properties, as well. The result of cooper strip test made with unadditized gas oil was 1B, so the strip was mild orange. The additives applied in 10-30 ppm concentration range inhibited the corrosion completely, so the classification of the strip after the test was 1A. The results of stricter rust prevention in ferrous parts confirmed the previous effects in copper strip test.

The lubricity improving efficiency of the additives was investigated in the range of 50-400 ppm in gas oil. The wear scar of the unadditized gas oil used as a reference was 530 μm . The results of the performance test showed that the additives based on vegetable oil had significant lubricity improving effect and by the application of 100 ppm additive, the limit of the standard could be reached (Fig. 3).

Table 7 Main properties of the final products

Properties	PIBFSI-1	PIBFSI-2	PIBFSI-3
Intermediate	PIBSAF-1	PIBSAF-2	PIBSAF-3
Acylating agent	TEPA	DETA	PEHA
Kinematic viscosity at 100 °C, mm ² /s	402,7	374,8	351,8
<i>3% additive in base oil</i>			
Kinematic viscosity at 40 °C, mm ² /s	35,8	37	36,8
Kinematic viscosity at 100 °C, mm ² /s	6,08	6,07	6,09
Extended viscosity index	116	110	111
Detergent Index, %	100	100	100
Washing Efficiency, mm	83	72	80
PDDE, %	82	76	80
<i>Corrosion properties (10-30 ppm additive in gas oil)</i>			
Copper strip corrosion	1A	1A	1A
Steel drift corrosion	0	0	0
<i>Lubricity tests (200 ppm additive in gas oil)</i>			
HFRR wear scar, μm	333	345	343
Fourball wear scar, μm [5]	713	730	726

TEPA: tetraethylene pentaamine; DETA: diethylene triamine; PEHA: pentaethylene hexaamine

The IR spectra and GPC of the final products were measured to determine the molecular structure of the additives. The number average molecular weight of the final product was 2200 ± 400 , the average polydispersity was 1.70; the average range of molecular weight was 12700-900. These mean that there were mono- and bis-succinimides containing bio-components as molecular-constituent synthesised from the previously shown intermediate products.

The characteristic vibrations of CH_2 and CH_3 - and the adsorption maximums of the olefinic bonds, as well as characteristic symmetric and asymmetric $-\text{C}-\text{O}-\text{C}-$ vibration of esters remained in the IR spectra of final products. Instead of the $\text{C}=\text{O}$ vibrations of anhydrides with five carbon atoms, the adsorption band of the imide can be observed in the range of $1700\text{-}1770\text{ cm}^{-1}$. The low intensity adsorption bands related to amides can be seen in the range of $1670\text{-}1630\text{ cm}^{-1}$. The results of the IR spectroscopy showed that

the fatty acid methyl esters are present in the synthesized additives as a building block of the molecule.

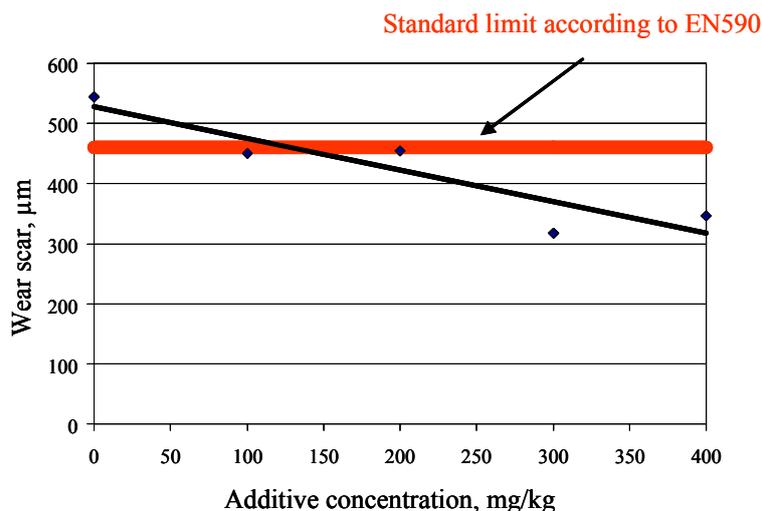


Figure 3 The lubricity properties of the selected PIBFSI-1 additives

3.3. Peugeot XUD-9 engine tests of the synthesized additives

It is a common experience that the results of laboratory and field tests method may be different; therefore the Peugeot XUD-9 tests (CEC F-23-A-01) of the chosen sample at both additive types were carried out. During the tests the concentration of the synthesized and reference additives was 90 vppm. Commercial additive package (Com. AP) containing succinic type deposit control additive was the reference. As it is shown on Figure 4 PIB-succinimid produced by radically initiated method had the highest nitrogen content and the best detergent property. The additives containing bio-components as molecular-constituent had better DD efficiency than the traditional succinimide, although the nitrogen content and the TBN of the samples were smaller. This means, that the polar end-group of FAME has an active role in the mechanism of detergent action.

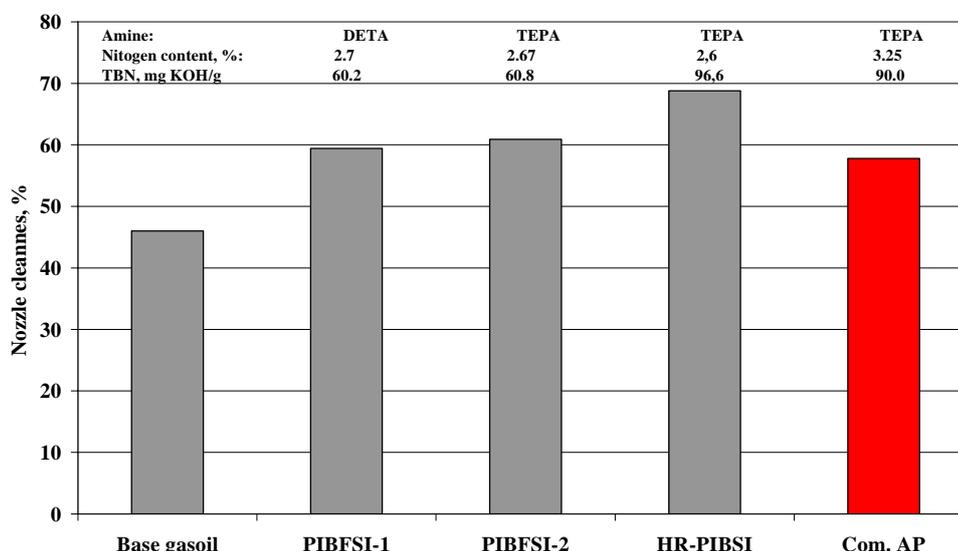


Figure 4 Results of the Peugeot XUD-9 test

4. Conclusions

Succinic anhydride derivatives from polyisobutylene ($\bar{M}_{nPIB} \sim 1000$) and maleic anhydride in the presence of radical initiator were synthesized, which were found to be suitable for producing diesel fuel additives. It was determined that fuel additives with improved DD efficiency can be produced from reaction of intermediers and polyethylene-polyamine according to well known methods of the synthesis of PIB-succinimides. The synthesized additive blended in diesel fuel can maintain cleanness of the injector nozzles of diesel

engines more efficiently than traditional polyisobutene-succinimides most frequently used as commercial deposit control additives.

It was realised, that with an original structure, alkyl-succinic anhydride containing bio-component as molecular-constituent can be synthesised from fatty acid methyl ester (FAME), polyisobutene and maleic anhydride in the presence of radical initiator. The selected intermediates containing bio-component as molecular-constituent were used to acylate polyethylene polyamines according to the investigated method applied for the synthesis of polyalkylene succinimides. The products were investigated by analytical and performance tests. Based on the results it can be concluded, that the DD efficiency of traditional succinimides could be achieved, moreover, in some cases exceeded. It was confirmed that the polar end-group of FAME has an active role in the mechanism of detergent action. The synthesized fuel additives had excellent corrosion inhibiting- and lubricity improving effects.

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- [6] ^1H NMR (400 MHz, CDCl_3) δ 7.60 – 6.55 (m, 0H), 2.46 (dd, $J = 23.1, 5.7, 1\text{H}$), 1.96 – 1.21 (m, 41H), 1.80 – 1.21 (m, 41H), 1.96 – -0.46 (m, 47H), 1.67 – -2.21 (m, 46H), 2.39 – -0.46 (m, 47H). ^{13}C NMR (101 MHz, CDCl_3) δ 180.51 – 160.94 (m, -8H), 128.90 (s, 1H), 128.07 (dd, $J = 28.4, 17.1, 1\text{H}$), 126.02 (s, 2H), 77.17 (d, $J = 31.9, 18\text{H}$), 76.69 (s, 7H), 76.66 – 76.29 (m, 2H), 59.69 (s, 2H), 59.69 – 58.53 (m, 32H), 58.48 – 57.57 (m, 3H), 39.94 – 38.71 (m, 2H), 38.42 – 37.54 (m, 36H), 33.80 – 30.25 (m, 98H), 30.66 – 30.25 (m, 2H), 30.66 – 30.07 (m, 2H), 29.16 – 27.77 (m, 1H), 26.49 (d, $J = 11.7, 1\text{H}$), 21.35 (s, 1H)
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- [9] ^1H NMR (400 MHz, CDCl_3) δ 7.24 (s, 0H), 6.53 – 6.50 (m, 0H), 5.33 (t, $J = 4.2, 1\text{H}$), 5.16 – 5.13 (m, 0H), 4.98 – 4.95 (m, 0H), 4.83 – 4.80 (m, 0H), 4.64 – 4.59 (m, 0H), 3.64 (s, 2H), 3.22 – 3.14 (m, 0H), 2.81 – 2.78 (m, 0H), 2.69 – 2.64 (m, 0H), 2.28 (t, $J = 7.5, 1\text{H}$), 1.99 (d, $J = 7.3, 3\text{H}$), 1.37 – 0.90 (m, 77H), 1.37 – 0.46 (m, 79H), 1.83 – 0.46 (m, 98H), 0.86 (dd, $J = 8.8, 5.0, 2\text{H}$). ^{13}C NMR (101 MHz, CDCl_3) δ 180.51 – 167.51 (m, -8H), 173.64 – 173.03 (m, 0H), 172.05 – 171.37 (m, 0H), 144.39 – 143.70 (m, 0H), 140.45 – 139.85 (m, 0H), 136.22 – 135.24 (m, -1H), 129.99 (s, 1H), 129.73 (s, 1H), 117.02 – 116.04 (m, 0H), 115.06 – 114.45 (m, -1H), 77.31 (s, 34H), 77.00 (s, 35H), 76.68 (s, 34H), 59.44 (d, $J = 13.6, 24\text{H}$), 58.82 (s, 2H), 58.19 (s, 2H), 51.43 (s, 2H), 38.09 (d, $J = 7.1, 24\text{H}$), 37.76 (s, 4H), 34.10 (s, 2H), 32.48 (d, $J = 14.6, 9\text{H}$), 31.89 (s, 2H), 31.43 – 31.01 (m, 54H), 30.76 (s, 9H), 29.36 (ddd, $J = 23.4, 15.6, 6.2, 18\text{H}$), 27.17 (d, $J = 5.6, 3\text{H}$), 24.93 (s, 2H), 22.67 (s, 2H), 14.10 (s, 2H)