SYNTHESIS OF VINYL ESTERS OF SOME DICARBOXYLIC ACIDS USING VINYL ACETATE

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Abstract: *In this work transvinylation reactions with vinyl acetate were carried out to synthesize vinyl esters of some dicarboxylic acids. The divinyl esters of dicarboxylic acids such as adipic, glutaric, succinic, phthalic, isophthalic and terephthalic were synthesized. The transvinylation reactions were conducted using activating reagents. The carboxylic acids were activated by 2-chloro-4,6-dimethoxy-1,3,5-triazine. Using potassium tert-butylate as a base, an intermediate was formed that easily transfers the vinyl group of vinyl acetate. This leads to the formation of divinyl esters. Based on the results of the conducted research, influence of such factors as solvent, temperature, time and molar ratios of the initial substances were analyzed. The optimal conditions for the process were determined.*

Key words: *Dicarboxylic acid, vinyl acetate, 2-chloro-4,6-dimethoxy-1,3,5-triazine, potassium tert-butylate, transvinylation reactions, active triazine ester of carboxylic acid, divinyl esters.*

Introduction

As global demand for sustainable and environmentally friendly polymer materials continues to rise, it is essential to address this need by effectively utilizing local resources with minimal energy consumption, low temperatures, and high reaction yields. This approach also leads to a reduction in material costs. Along with the polymerization process, localizing the synthesis of their monomers and additives is also recognized as a key challenge [1, 2].

Vinyl esters are important compounds that find wide applications in various fields. Carboxylic acid vinyl esters contain both a double bond and an ester group in their molecules, allowing them to undergo various chemical transformations. They are key reagents in organic and polymer synthesis. Vinyl esters of higher carboxylic acids have economic importance as monomers in the production of copolymers. Vinyl esters can act as crosslinking agents in polymer chains, enhancing the mechanical properties and stability of the resulting materials. They can be copolymerized to obtain polymer materials with desirable properties such as flexibility, toughness and chemical resistance, which are crucial in producing high-performance coatings, composite materials, adhesives and paints [3-5].

The synthesis of carboxylic acid vinyl esters began in the early 20th century using mercury salts as catalysts. Today several methods for vinylation have been developed, and a variety of 3d metal catalysts can be used with high efficiency in both homogeneous and heterogeneous catalytic processes. Under mild conditions, the coupling reactions of carboxylic acids with alkynes, catalyzed by transition metals, are regarded as the most effective method for synthesizing vinyl esters [6, 7]. In recent years, numerous catalysts such as Zn, Ru, Pd, Au, Ir, Rh, Pt, Re and Hg have been developed, allowing for the direct utilization of carboxylic acids as active centers without requiring additional steps. However, the high cost of catalysts and the complexity of acetylene vinylation necessitate the use of simpler reaction conditions [8-10].

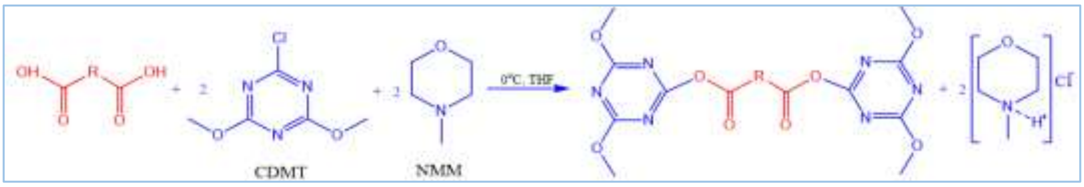
Thus, optimal synthesis pathways for vinyl esters need to be developed, utilizing minimal reaction steps and locally available raw materials. There is a need for an economically viable process to produce vinyl esters of carboxylic acids. The challenge lies in improving product yield through the selection of an appropriate catalyst system. Therefore, *in this study,* transvinylation reactions were carried out using activating reagents to facilitate the process.

Experimental part

Materials and methods. In industry there are two main approaches for synthesizing vinyl compounds. The first approach involves homogeneous or heterogeneous catalytic reactions based on acetylene, carried out under high pressure and temperature. In this method, carboxylic acids react with acetylene to form complex vinyl esters. The second approach is based on vinyl exchange reactions involving vinyl acetate. This method does not require catalysts and uses active derivatives of carboxylic acids to facilitate the vinyl exchange reaction under mild conditions. Various production technologies have been developed in the industry for both methods [11, 12].

In the research, the vinyl exchange reaction was carried out in a homogeneous medium at low temperature without the use of metal catalysts, utilizing 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) and potassium tert-butylate (t-BuOK) as reagents. This approach is based on the easy reaction of the intermediate active triazine ester of the carboxylic acid and potassium vinyloxide. The general reaction scheme can be represented as follows [13-15].

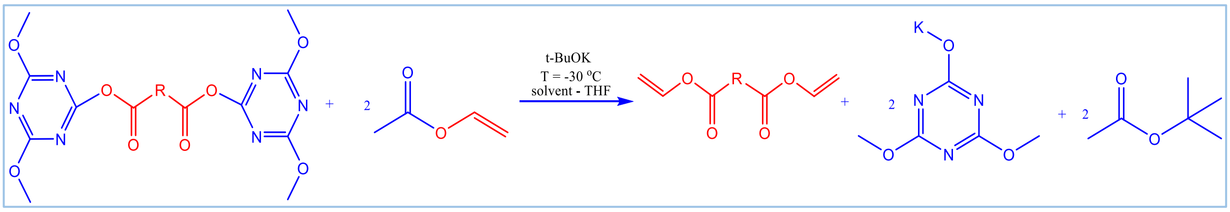
The selected dicarboxylic acids react with CDMT and N-methyl morpholine (NMM) to form the acid-active triazine ester, bis(4,6-dimethoxy-1,3,5-triazine-2-yl) adipate. Additionally, N-methyl morpholine hydrochloride is also produced as a byproduct (Scheme 1).



Scheme 1

Vinyl acetate is activated with *t*-BuOK. An unstable compound, potassium vinyloxide, is formed, which transfers the vinyl group. Tertiary butyl acetate is produced as a byproduct in the reaction. During the reaction, the mixture turns brown and needs to be cooled.

The two mixtures formed above—the active triazine ester of the dicarboxylic acid and potassium vinyloxide—react with each other to produce the divinyl ester of dicarboxylic acid and the potassium salt of 2-oxo-4,6-dimethoxy-1,3,5-triazine (Scheme 2).



Scheme 2

Dicarboxylic acid (0.01 mole) and CDMT (0.02 mole) were suspended in 30 ml of tetrahydrofuran (THF) and cooled to 0°C. While stirring, NMM (0.02 mole) was added by dropwise and the mixture was stirred for 30 minutes. *t*-BuOK (0.02 mole) and THF (30 ml) were added to the second container, and the suspension solution was cooled to -30°C. While stirring, vinyl acetate (0.02 mole) was added dropwise using a dropping funnel. The resulting two solutions were then combined and stirred at -30°C for 2 hours. Then 30 ml of a 5% NH_4Cl solution was added to the mixture to remove potassium ions. The mixture was extracted with methyl tert-butyl ether (t-BuOMe). The extract was washed with $NaHCO_3$ (0.5 M), distilled water, $NaHSO_4$ (0.5 M) and distilled water. It was then dried over Na_2SO_4 and the solvent was evaporated under vacuum. The product was purified by column chromatography using a 5:1 hexane/ethyl acetate. The obtained vinyl esters were analyzed using IR, ^{1}H-NMR, ^{13}C-NMR, and GC-MS.

Adipic acid divinyl ester. Yield 82%; IR: 1132.21 (-C-O-C-), 1417.68 (=CH, def.), 1645.28 ($CH=CH_2$), 1749.44 (>C=O), 2945.30 (>CH_2), 3091.89 (=CH, val.). ^{1}H-NMR: (400 MGs, CD_3 OD, δ, m.u.): δ 1.56 (4H, quint, methylene, β -CH_2-), 2.35 (4H, t, methylene, α -CH_2-), 5.00 (2H, dd, vinyl, sis CH_2), 5.12 (2H, dd, vinyl, trans CH_2), 7.44 (2H, dd, vinyl, -CH). ^{13}C-NMR: (150 MGs, CD_3OD, δ): δ 24.88 (2C, methylene, β CH_2), 34.07 (2C, methylene, α CH_2), 97.891 (2C, vinyl, CH_2), 142.328 (2C, vinyl, CH), 171.72 (2C, carbonyl, -C(O)O-). GC-MS: m/z calculated 198.09, $C_{10}H_{14}O_4^+$, found 199.3.

Glutaric acid divinyl ester. Yield 80%; IR: 1090.75 (-C-O-C-), 1436.97 (=CH, def.), 1667.46 ($CH=CH_2$), 1722.43 (>C=O), 2868.15 (>CH_2), 2928.91 (=CH, val.). ^{1}H NMR: (400 MGs, CD_3OD, δ, m.u.): δ 1.82 (2H, quint, methylene, β -CH_2-), 2.38 (4H, t, methylene, α -CH_2-), 5.00 (dd, vinyl, sis CH_2), 5.12 (dd, vinyl, trans CH_2), 7.44 (2H, dd, vinyl, -CH).^{13}C-NMR: (150 MGs, CD_3OD, δ): δ 19.7 (1C, methylene, β CH_2), 33.9 (2C, methylene, α CH_2), 97.3 (2C, vinyl, CH), 141.3 (2C, vinyl, CH_2), 170.6 (2C, carbonyl, -C(O)O-). GC-MS: m/z calculated 184.07, $C_9H_{12}O_4^+$, found 186.9.

Succinic acid divinyl ester. Yield 77%; ^{1}H NMR: (400 MGs, CD_3OD, δ, m.u.): δ 2.846 (4H, t, methylene, CH_2), 5.00 (4H, dd, vinyl, sis CH_2), 5.118 (2H, dd, vinyl, trans CH_2), 7.437 (2H, dd, vinil, -CH).^{13}C NMR: (150 MGs, CD_3OD, δ): δ 29.1 (2C, methylene, CH_2), 97.3 (2C, vinyl, CH), 141.33 (2C, vinyl, CH_2), 170.62 (2C, carbonyl, -C(O)O-).

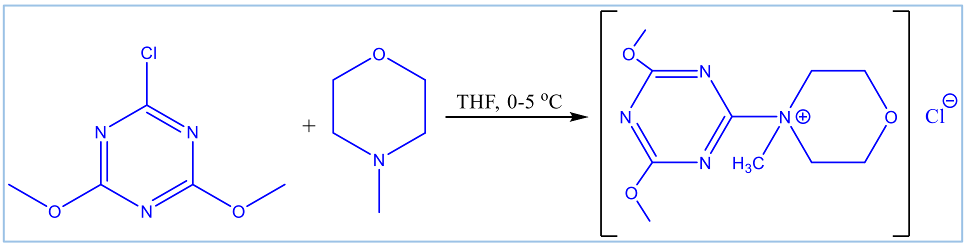
Phthalic acid divinyl ester. Yield 65%; ^{1}H-NMR (400 MGs, CD_3OD, δ, m.u.) δ 7.98 (2H, dd,), 7.67 (2H, dd), 7.48 (2H, dd), 4.90 (2H, dd), 4.59 (2H, dd). ^{13}C NMR (150 MGs, CD_3OD, δ) δ 98.08 (2C, vinyl, CH_2), 129.69 (2C, Ar. C-3,6), 129.99 (2C, Ar. C-1,2), 130.62 (2C, Ar. C-4,5), 139.95 (2C, vinyl, -CH), 164.70 (2C, carbonyl, -C(O)O-).

Isophthalic acid divinyl ester. Yield 68%; IR: 1089.78 (-C-O-C-), 1436.97 (=CH, def.), 1667.46 ($CH=CH_2$), 1713.75 (>C=O), 2864.4 (>CH_2), 2926.98 (=CH, val.). ^{1}H NMR: (400 MGs, CD_3OD, δ, m.u.): δ 5.03 (2H, dd, vinyl, sis CH_2), 5.13 (2H, dd, vinyl, trans CH_2), 7.44 (2H, dd, vinyl, -CH), 7.68 (1H, td, Ar. C-5), 8.15 (2H, dt, Ar. C-4,6), 8.61 (1H, td, Ar. C-2). ^{13}C-NMR: (150 MGs, CD_3OD, δ): δ 97.3 (2C, vinil, CH_2), 126.0 (2C, Ar.xal. C-1,3), 128.0 (1C, Ar. C-5), 129.7 (2C, Ar. C-4,6), 131.3 (1C, Ar. C-2), 141.3 (2C, vinyl, -CH), 163.5 (2C, carbonyl, -C(O)O-).

Therephthalic acid divinyl ester. Yield 70%; ^{1}H-NMR: (400 MGs, CD_3OD, δ, m.u.): δ 5.027 (2H, dd, vinyl, sis CH_2), 5.135 (2H, dd, vinyl, trans CH_2), 7.443 (2H, dd, vinyl, -CH), 7.766 (4H, ddd, Ar. C-2,3,4,6). ^{13}C-NMR: (150 MGs, CD_3OD, δ): δ 97.3 (2C, vinyl, CH_2), 129.5 (2C, Ar. C-1,4), 129.6 (4C, Ar. C-2,3,5,6), 141.3 (2C, vinyl, -CH), 163.49 (2C, carbonyl, -C(O)O-).

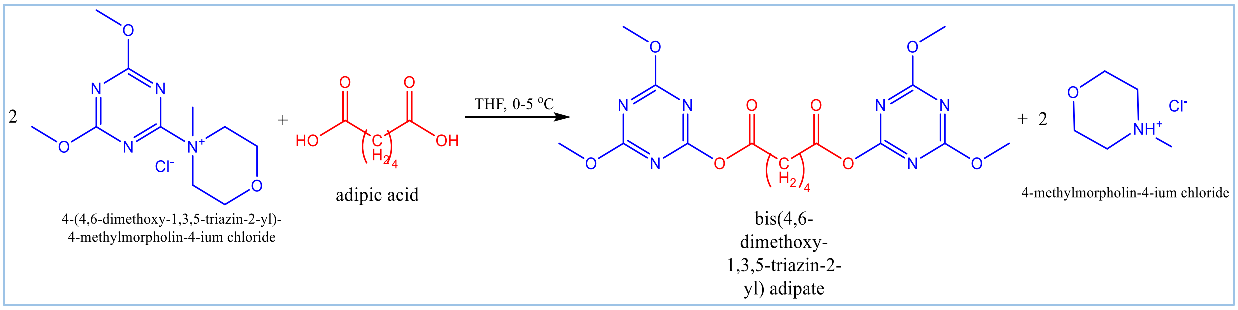
Results and discussion

A review of the literature indicates that in this method, vinyl exchange proceeds through a nucleophilic attack. The vinyl exchange reaction mechanism with vinyl acetate for dicarboxylic acids (adipic, glutaric, succinic, phthalic, isophthalic, and terephthalic acids) has been proposed based on adipic acid. The process involves two main stages in transvinylation reactions, facilitated by specific activating reagents. CDMT is a commonly used coupling reagent for activating carboxylic acids. In this case, CDMT reacts with the carboxylic acids to form an intermediate product and makes the carboxyl group susceptible to nucleophilic attack. The activation stage is crucial as it enhances the reactivity of the carboxyl group, facilitating the subsequent vinylation process. Initially, CDMT reacts with NMM to form an intermediate active complex (Scheme 3).



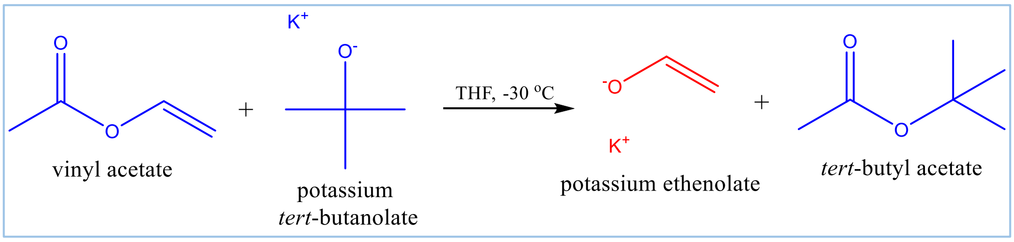
Scheme 3

The resulting complex reacts with adipic acid with formation of acid-active triazine ester, bis(4,6-dimethoxy-1,3,5-triazine-2-yl) adipate (Scheme 4).



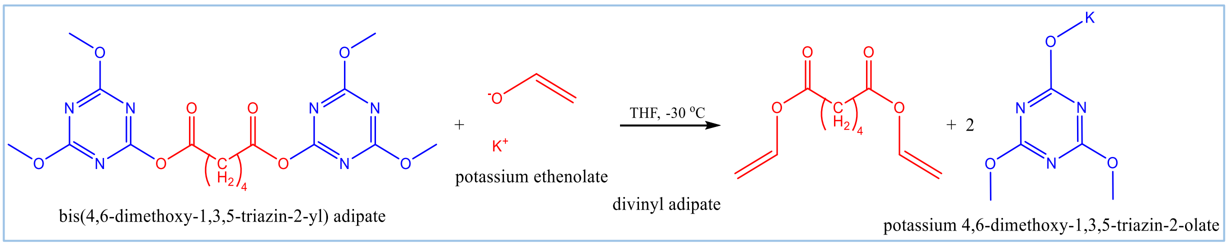
Scheme 4

Subsequently, the reaction begins with the nucleophilic attack of t-BuOK on vinyl acetate, forming an active vinyl-oxy intermediate ion (see Scheme 5). t-BuOK acts as a strong base to deprotonate the acetate, leading to the formation of the vinyl intermediate product. This intermediate then reacts with the activated carboxylic acid triazine ester to produce the desired vinyl ester product. The use of KOtBu ensures effective vinyl exchange and aids in the formation of the final product.



Scheme 5

During the reaction process, the potassium vinyloxide formed reacts with the acid-active triazine ester to produce the corresponding vinyl ester (Scheme 6). In this stage, vinyl acetate undergoes to vinyl exchange reaction with the activated carboxylic acid.



Scheme 6

The transvinylation reaction based on triazine is an exothermic reaction, achieving high product yields at -30°C. When the temperature was lowered to -40°C, was observed the reaction mixture freezing (suspension).

The reaction was conducted in several solvents to study the effect of solvents on the reaction yield. Factors considered in solvent selection included the solvent's polarity, the ability to prevent freezing of the reaction mixture down to -40°C, and the solvent's tendency to react with reagents (e.g., with t-BuOK). Since the reaction is exothermic, experiments were carried out at low temperatures. High yields were achieved when the reaction was carried out in tetrahydrofuran (THF) and at the temperature -30°C (Table 1).

Table 1. Effect of temperature and solvents on the products of transvinylation reaction of dicarboxylic acids with vinyl acetate (t = 1 h, mole ratio dicarboxylic acid:vinyl acetate is 1:2)

Divinyl Ester	Solvent								
	THF			**DCM**			**ACN**		
	Temprature (°C)								
	-10°C	*-20°C*	*-30°C*	*-10°C*	*-20°C*	*-30°C*	*-10°C*	*-20°C*	*-30°C*
	Yield of products (%)								
Adipate	43	49	52	36	38	42	25	27	29
Glutarate	40	46	50	34	34	38	21	24	27
Succinate	38	44	47	31	33	35	19	20	28
Therephthalate	37	42	46	29	29	33	17	20	24
Isophthalate	34	40	44	26	27	30	18	23	24
Phthalate	29	36	40	21	23	25	-	-	20

Based on the conducted studies, the reaction duration for vinyl exchange reactions was investigated. The research showed that the best results were achieved with a reaction time of 2 hours when experiments were conducted for 1, 2, 3, and 4 hours (Table 2). When the reaction time was extended beyond 2 hours, a decrease in product yield was observed, which can be explained by an increase in the conversion of starting materials but a decrease in the selectivity of the reaction. The formation of additional products negatively impacts the overall yield.

Table 2. Effect of time on the products of transvinylation reaction of dicarboxylic acids with vinyl acetate (T = -30, solvent – THF, mole ratio dicarboxylic acid and vinyl acetate is 1:2)

Divinyl Ester	Time (hour)			
	1 h	2 h	3 h	4 h
	Yield of products (%)			
Adipate	52	61	55	50
Glutarate	50	58	54	51
Succinate	47	57	50	45
Therephthalate	46	54	51	30
Isophthalate	44	52	49	40
Phthalate	40	48	48	32

When the ratio of dicarboxylic acid to vinyl acetate is 1:2.4, increasing product yield was observed (Table 3). However, as the molar ratio is changed from 1:2.4 to 1:2.6, the reaction yield has decreased, what can be explained by the formation of additional vinyl by-products, which negatively impacts on the overall yield.

Table 3. Effect of mole ratio (dicarboxylic acid:vinyl acetate) on the products of transvinylation reaction of dicarboxylic acids with vinyl acetate (T = -30°C, t = 2 h, solvent – THF)

Divinyl Ester	Molar ratio (dicarboxylic acid/vinyl acetate)			
	1:2	**1:2.2**	**1:2.4**	**1:2.6**
	Yield of products (%)			
Adipate	61	69	82	70
Glutarate	58	66	80	67
Succinate	57	65	77	60
Therephthalate	54	65	70	62
Isophthalate	52	64	68	58
Phthalate	48	61	65	59

The spectrums of the synthesized divinyl esters were obtained and analyzed. As an example, the spectral analysis of the divinyl adipate is provided.

In the IR spectrum of the divinyl ester derived from adipic acid, the following observations were made. The absorption band for the hydroxyl group is absent, indicating its removal. CH_2 groups exhibit absorption bands at 2956.39-2878.09 cm^{-1}, with a characteristic bending vibration at 1364.78 cm^{-1}**.** Carbonyl group shown an absorption band at 1749.19 cm^{-1}. Ester bond (-C-O-C-) was observed in the absorption range of 1128.55 cm^{-1}. The =CH bond in the vinyl group appeared at 3091.89 cm^{-1} and the deformation vibration appeared at 1417.68 cm^{-1}. The double bond ($CH=CH_2$) in the vinyl group appeared at 1645.28 cm^{-1} (Fig. 1).

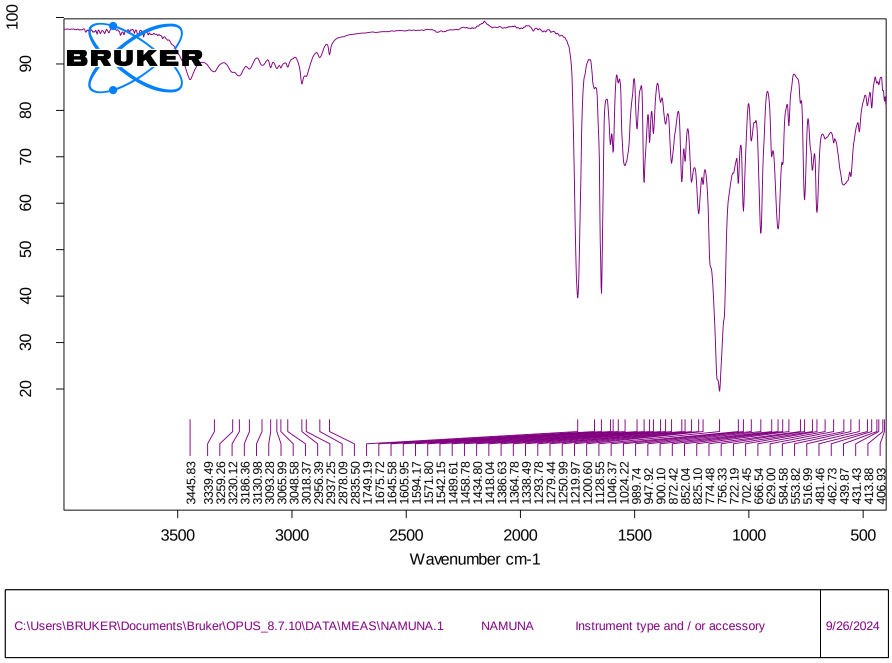


Fig. 1. IR-spectrum of divinyl adipate.

In the ^{1}H-NMR spectrum of the divinyl ester of adipic acid, the multiplet signal of protons attached to the 3rd and 4th carbons in relation to the carboxyl group of adipic acid was observed at 1.60-1.64 ppm and the triplet signal of protons attached to the 2nd and 5th carbons was observed at 2.36-2.40 ppm. The doublet-doublet signal of two protons in the vinyl group ($=CH_2$) was observed at 4.5-4.8 ppm and the quartet signal of one proton (CH=) atom in the vinyl group was observed at 7.18-7.24 ppm (Fig. 2).

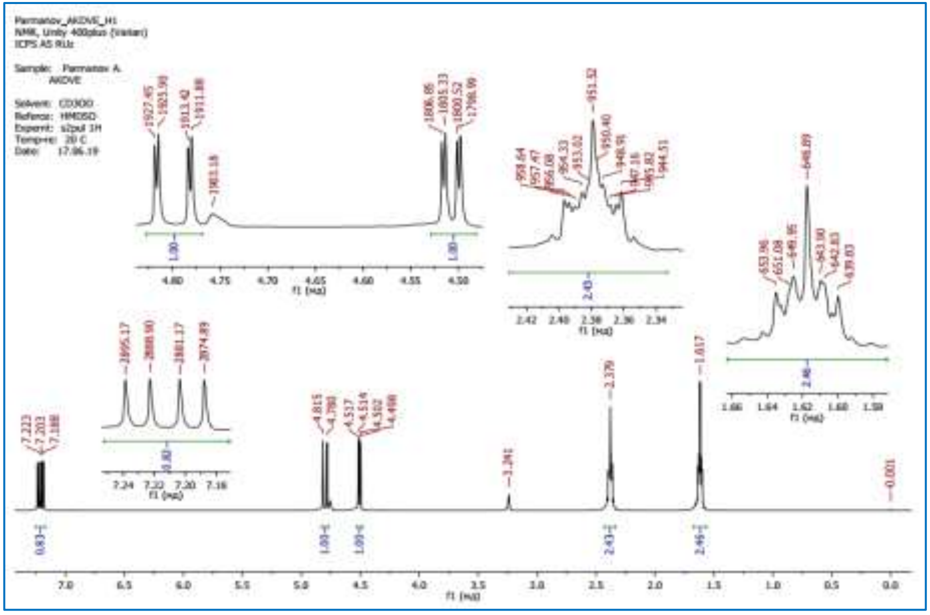


Fig. 2. ^{1}H-NMR spectrum of divinyl adipate.

In the ^{13}C-NMR spectrum of the divinyl ester of adipic acid, carbon atoms at positions 3 and 4 are observed at 24.9 ppm, while carbon atoms at positions 2 and 5 are noted at 34 ppm. Carbon atoms at positions 1 and 6 are detected at 171.7 ppm. The carbon atoms in the vinyl group appear at 142.3 ppm (for –CH=) and 97.9 ppm (for $=CH_2$) (Fig. 3).

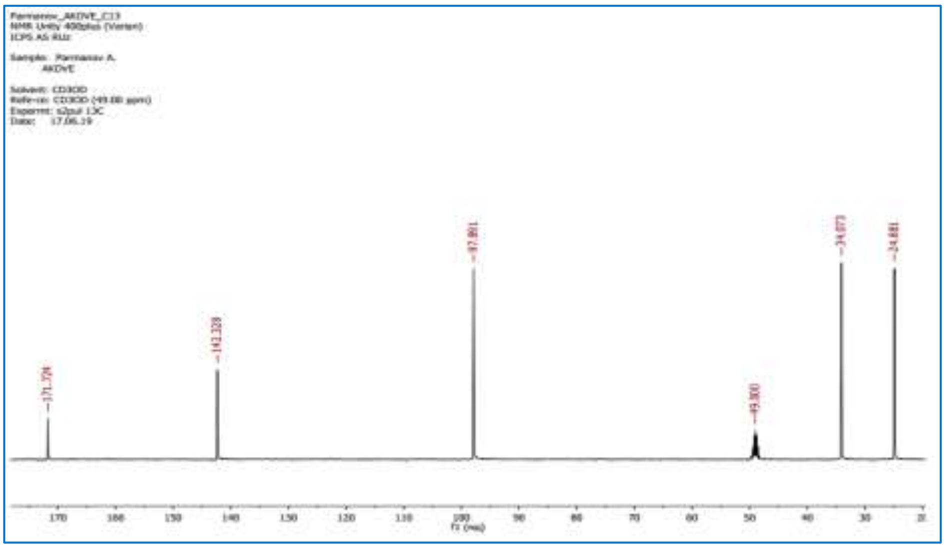


Fig. 3. ^{13}C-NMR spectrum of divinyl adipate.

When the vinyl ester of adipic acid was introduced into the mass spectrometer, a molecular ion with m/z = 199.3 for the vinyl ester was detected under the chosen conditions. Subsequently, the molecular ion of the vinyl ester fragmented into various radical and ion species, including m/z = 185, 167, 148.9, 133.5, 121, 114.9, 92.7, and 77.2 (Fig. 4).

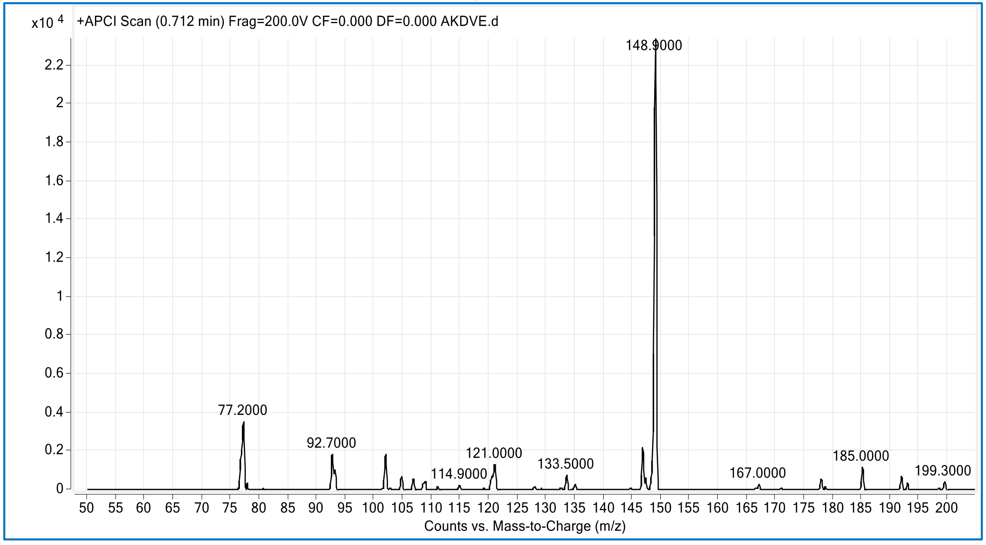


Fig. 4. Xromato-mass spectrum of divinyl adipate.

Conclusions

In this study, vinyl esters of dicarboxylic acids were synthesized at low temperatures using activating reagents. Active triazine esters of adipic, glutaric, succinic, phthalic, isophthalic, and terephthalic acids were prepared with 2-chloro-4,6-dimethoxy-1,3,5-triazine. The intermediate potassium vinylate, which transfers the vinyl group, was obtained by vinyl exchange reaction of tertiary butyl acetate and vinyl acetate. These activation-stage products were then used to synthesize vinyl esters. The reactions were carried out in tetrahydrofuran solution, with optimal conditions determined to be -30°C, atmospheric pressure, a reaction time 2 hours, and a molar ratio 1:2.4 for the initial substances (dicarboxylic acid and vinyl acetate).

The analysis of the obtained results shows that the activity of the selected dicarboxylic acids in the vinyl exchange reaction with vinyl acetate follows the order: phthalic < isophthalic < terephthalic < succinic < glutaric < adipic acid. Under the determined optimal conditions, the best result was achieved with the production of adipic acid divinyl ester, reaching with yield 82%.

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