



AN OXIRANE – PENDANT – GROUPS COPOLYMER, ACTIVE AS SYNTAN IN LEATHER PROCESSING♦

Stelian Sergiu Maier*, Vasilica Maier, Melinda Pruneanu

*„Gh. Asachi” Technical University, Blvd. D. Mangeron 67, 700050 Iași,
Romania, *Tel. 0040 232 279 850, E-mail: smaier@ch.tuiasi.ro*

Abstract: The paper presents the synthesis principles of an oligomeric reactive tanning agent useful in leather processing, and the practical synthesis guidelines for a poly[(glycidyl-methacrylate) - co - (fumaric acid) - co - (maleic acid)]. The synthesis pathway is straightforward and avoids the expensive anionic copolymerization techniques but requires the pursuing of a severe procedure for reactions control during the molecular building stages.

Keywords: *pendant oxirane, reactive copolymer, oligomer, syntan, leather*

INTRODUCTION

In order to act as a tanning agent in leather processing, a synthesis macromolecular compound must meet several requirements:

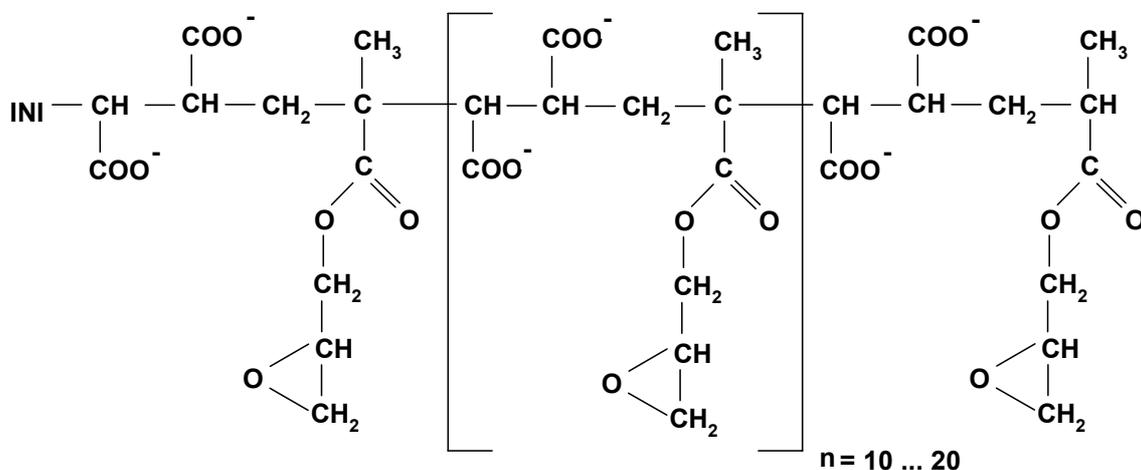
- medium to low molecular mass, permitting the penetration inside the dermal microstructure, either at a molecular level or at a molecular aggregates level;
- the ability to interact with the chemical functions of the side amino acid chains and set up chemical bonds or strong and stable physical interactions;
- good solubility at usual pH values of processing floats;

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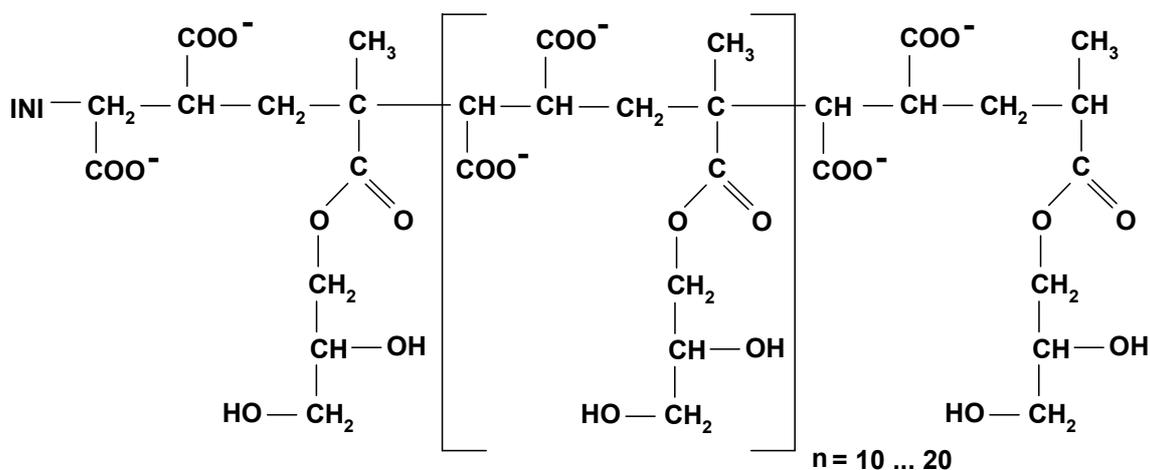
- the ability to change the level (and even the type) of reactivity towards the dermal proteins through simple variation of the technological parameters of floats.

Reactive macromolecular compounds from the oligomeric class are potential tanning agents, that are often being used for the achievement of some tanning (hydrothermal stabilization associated with filling and shading effects) or retanning (advanced firmness, differential filling, hydrophilicity adjustment, pseudo-greasing, supplemental functionalization) special effects. Among these oligomers, those bearing reactive oxirane groups are less studied, due to the difficulties related to their synthesis and to the formulation of the corresponding commercial products, even if their affinity for leather is very close to those exhibited by linear dialdehydes.

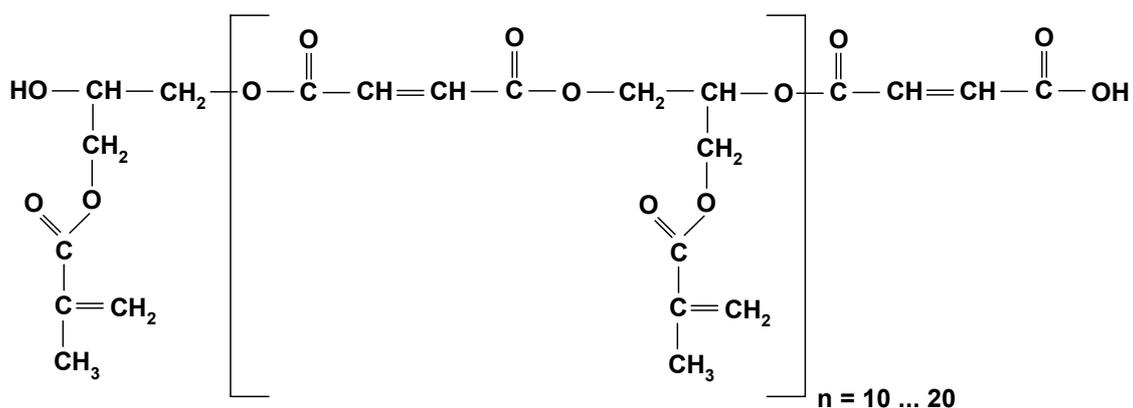
The aim of this paper is the synthesis of a copolymer between glycidyl-methacrylate and maleic anhydride hydrolysis product (mainly represented by the fumaric acid salt) through a radicalic mechanism, having the following theoretical structure:



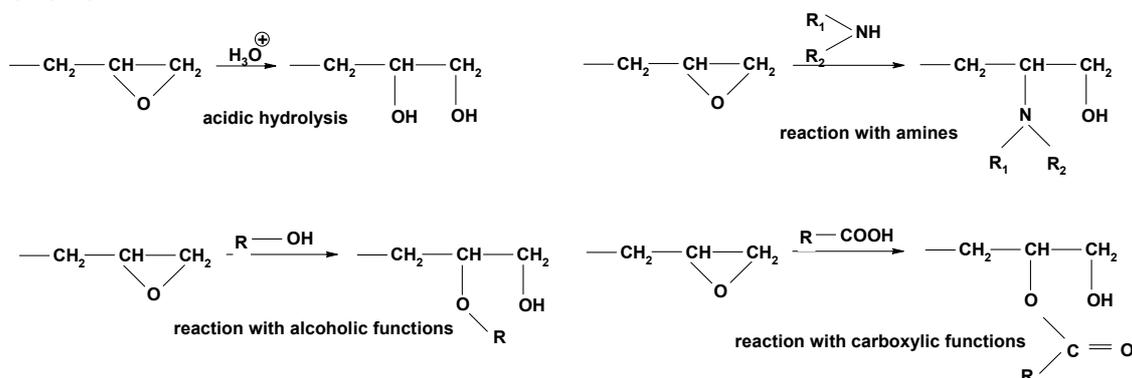
The synthesis through radicalic mechanism unavoidably leads to the formation of molecular species with diminished functionality, due to the inactivation of the oxirane functions:



or even extensively altered (as a consequence of severe modification of radical attack positions and subsequent propagation):



The oxirane group degradation can also proceed *via* reactions with water or with the co-monomer, the initiator, initiator degradation products or impurities found in the reaction media, and results in other interfering products in the reaction mass [1 – 3]. For this reason, at the end of the synthesis and during product keeping, the synthesis product will exhibit high polydispersity of structural and composition characteristics. Despite this, due to the high reactivity of oxirane functions, the presence of even few unchanged reactive groups can provide the expected tanning effect. The reactions of the oxirane function with the protein groups and the possible inactivation reactions are given as it follows:



Owing to the presence of carboxyl and hydroxyl functions on the oligomer chains (arising from the co-monomer and from hydrolysis, respectively), three of the four reactions given above can take place during keeping in ordinary conditions in the absence of a stabilizer, which leads to reticulations that result in loss of the active substance solubility, finally reflected in the sedimentation of the finely dispersed initial synthesis product. The product stability can be achieved in the formulation stage, which can prove to be more difficult than the synthesis itself.

SYNTHESIS PROTOCOL OF THE TARGET PRODUCT

The experimental receipt for the obtaining of the oxirane oligomer stipulates the use of the following two co-monomers: **(A)** glycidyl-methacrylate and **(B)** the sodium salt of the maleic anhydride hydrolysis product. The chose of this reaction couple was dictated

by: (1) minimization of unwanted reactions of the oxirane function with the acid groups of the co-monomer; (2) providing the active product with hydrophilicity in the synthesis stage, thus making a subsequent hydrolysis of the anhydride ring redundant. This starting composition achieves the most reasonable compromise between the co-monomers costs and the efficiency of the synthesis product as potential tanning agent, assessed in terms of maximization of the number of free oxirane functions on the polymeric chain, unaltered during the synthesis step.

From a theoretical point of view, the initial ratio between the two co-polymers was established following the **Q-e scheme** (elaborated by Alfrey and Price). The values of the coefficients used for the calculation of the theoretical composition of the radical copolymerization product are given in Tables 1 and 2. Data concerning the glycidyl-methacrylate – maleic anhydride couple are given comparatively.

Table 1. Values of the monomers characteristics used in the **Q-e** scheme

Monomer	Characteristics	
	Q	e
Glycidyl-methacrylate	0.96	0.20
Maleic acid*	0.34	1.14
Maleic anhydride	0.23	2.25

* - Q and e values are taken from reference [4].

Table 2. Values of the reactivity ratios calculated for the possible comonomer couples

Co-monomer couple	Values calculated according to the Q – e scheme					
	r ₁	r ₂	1 / r ₁	1 / r ₂	r ₁ r ₂	1 / r ₁ r ₂
A - Glycidyl-methacrylate B - Maleic acid	3.407	0.121	0.293	8.264	0.412	2.427
A - Glycidyl-methacrylate C - Maleic anhydride	6.298	2.738 · 10 ⁻³	0.159	446.86	0.015	66.667

It can be seen that in comparison with the maleic anhydride, the maleic acid (and most likely its sodium salt as well) is a weaker electron acceptor (see e value) and its double bond can strongly localize the π electrons (see Q value). Consequently, the kinetics of the copolymerization reaction in which the maleic acid and/or its fumaric acid conformer take part will be slower and consequently more favorable to oligomers formation. On the other hand, the tacticity of the glycidyl-methacrylate – maleic acid couple will be less regular than those of the glycidyl-methacrylate – maleic anhydride couple (see r₂ couple). The inverse ratio of the two copolymerization products (1 / r₁r₂) comes to ascertain this fact [5]. Hence, the copolymer between the glycidyl methacrylate and the disodium salt of the maleic acid will be, in all probability, not an alternant but a statistic one, while the glycidyl-methacrylate – maleic anhydride couple will give raise to alternant copolymers.

Figures 1 and 2 depict the theoretical composition of the above mentioned copolymers, as a function of the molar ratios of co-monomers in the reaction mass. (A Java applet from the address referred in [6] was used).

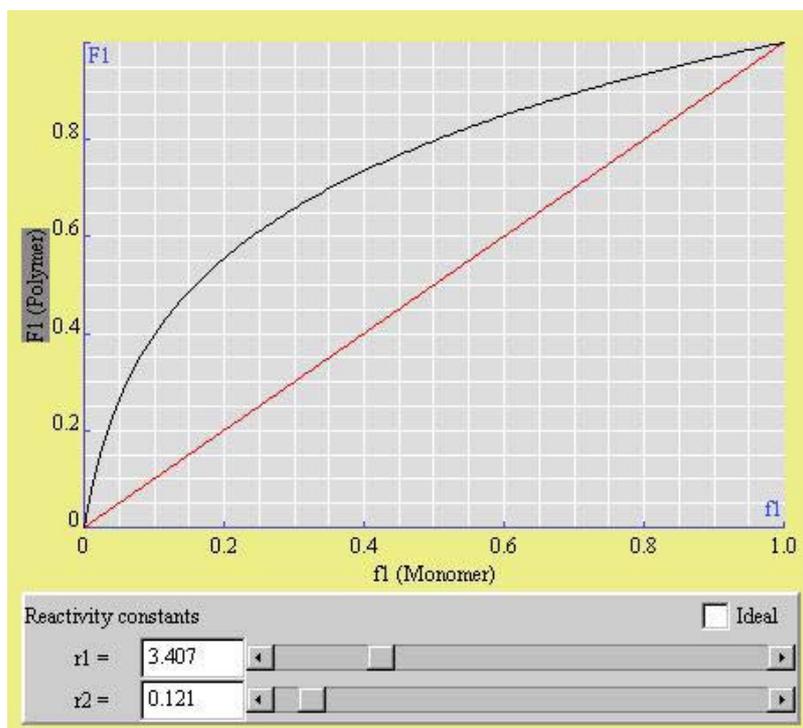


Figure 1. The dependence between the glycidyl-methacrylate–maleic acid copolymer composition and the starting composition of the co-monomer mixture

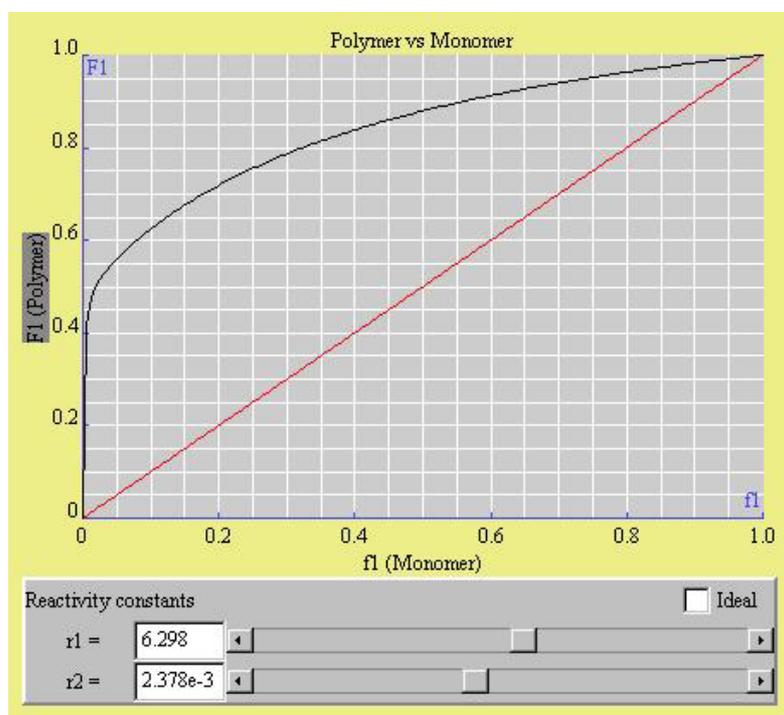


Figure 2. The dependence between the glycidyl-methacrylate–maleic anhydride copolymer composition and the starting composition of the co-monomer mixture

The values of the glycidyl-methacrylate molar ratio in the initial reaction mixture (f_1) are given on the x-axis, while on the ordinate are given the values of the theoretical molar ratio of the same co-monomer in the polymer (F_1), calculated on the condition that the ratio between the two co-monomers remains almost constant during the radicalic propagation stage. When comparing the two diagrams, one can see that starting with a 1:1 molar ratio, the couple glycidyl-methacrylate – maleic acid produces 0.75 oxirane functions on the copolymer chain, while the glycidyl-methacrylate – maleic anhydride couple is more active and produces 0.87 oxiranes. Therefore, the oxirane functionality is lower and favorable to prolonged stability of the reaction product.

The theoretical initial molar ratio between the selected co-monomers (glycidyl-methacrylate and the disodium salt of the maleic acid) in the reaction mixture should be 0.15:0.85, in order to obtain a 1:1 ratio in the reaction product. We consider that in practice the starting molar ratio should be very close to equimolarity and even slightly favorable to the maleic anhydride hydrolysis product. Under these circumstances, the formation of portions of block copolymer mainly constituted from salified carboxyl unities is theoretically possible (see the differences between the $1/r_1$ and $1/r_2$ ratios). The steric remoteness between the oxirane and carboxyl mer units during the radical propagation, as well as the statistical hindrance to the interaction between the two co-monomers will facilitate the remaining on the oligomer chain of unaltered oxirane functions, which are responsible for the potential tanning action of the reaction product. Consequent to laboratory scale synthesis tests, a working protocol was conceived, that provides oligomer optimal yields and solubility characteristics that enable the reaction product to be used as potential tanning agent. The reactants employed in synthesis are given in Table 4; the experimental molar ratios that proved to be the most favorable to the obtaining of a product with tanning potentialities are given in Table 3.

Table 3. Chemicals used in the synthesis of the oligomer with tanning potentialities

Reactant		Molecular weight (Da)	Density (g/cm ³)
Reaction media		Water	18.00
Starting co-monomers	M ₁	Glycidyl methacrylate	142.20
	M ₂	Maleic anhydride	98.06
Initiator		4,4'-azobis(2-cyanovaleric) Acid, CAS 2638-94-0	280.29
Nonionic emulsifying agent		Emulsifier ABEX UV/30 Rhône-Poulenc	(not specified by the producer)
Hydrolyzing agent		Sodium hydroxide R.G., solution (50 %)	40.0
Neutralizing agent for pH adjusting		Hydrochloric acid R.G., solution (37 %)	36.5
Inhibitor		Carbon tetrachloride	153.82
			1.5900

The synthesis protocol of the product with block copolymer sections consists of seven stages, as it follows: (1) preparation of the co-monomer M¹ through emulsification in the presence of a inhibitor; (2) preparation of the co-monomer M₂, through partial hydrolysis of maleic anhydride to maleic/fumaric acid, followed by salting out at neutral pH; (3) preparation of the radical initiator by dissolving in water followed by ageing and degasification; (4) making-up the starting reaction mass and including the M₂ co-

monomer and the initiator; (5) adding the co-monomer M_1 through quick injection; (6) copolymerization completion; (7) post-processing the reaction mass.

Table 4. Experimental optimal ratios and amounts of reactants for the obtaining of oxirane oligomer with block copolymer sections

Optimal ratios and amounts		
Imposed molar / volume ratios	M1 – Glycidyl methacrylate	1 : 2.5
	M2 – Maleic anhydride	
	Solvent (volumes)	
	Monomers mixture (volumes)	50 : 1
	Initiators	
	Monomers mixture	0.08 : 1
	Inhibitors	
	Monomers mixture	
	Alkali agent (volumes)	1.85 : 1
	Monomer 2 (volumes)	
	Neutralizing agent	0.025 : 1
	Monomer 2	
Emulsifier (volumes)	0.010 : 1	
Monomer M1 (volumes)		
Constituents of the reaction media		Dosage
Solvent	Water	in several steps
Monomers	M1 – Glycidyl-methacrylate	0.0759 mols
	M2 – maleic anhydride	0.1669 mols
Initiators	4,4'-azobis(2-cyanovaleric) acid	0.0194 mols
Auxiliaries	Sodium hydroxide	2.3 mL of 0.2 M sol.
	Emulsifier ABEX	0.3 mL
	Carbon tetrachloride	0.45 mols
Other chemicals	Hydrochloric acid	1 M solution

The specific manners in which these stages are prepared and conducted dictate the inactivation extent of the oxirane functions, the co-monomers enchainment regularity and the medium length of copolymer chains.

The laboratory procedure guidelines for the preparation of the oxirane-pendant-groups copolymer are given below:

- the synthesis is carried out in a glass kettle-type reaction vessel, with sealing cap and three polished necks, to which a stirrer, a thermometer and a dosing system are connected, respectively; the vessel is introduced in a water bath thermostat;
- *preparation of co-monomer M_1* : 10.3 mL of glycidyl-methacrylate are introduced in a round-bottom vessel, then 0.1 mL carbon tetrachloride and 0.3 mL emulsifier are added under stirring and the resulting mixture is thermostated at 45 °C ; 50 mL of deionized water, preheated at 45 °C is dripped added under vigorous mixing, until emulsification is achieved;
- *preparation of co-monomer M_2* : 16.36 g maleic anhydride is dissolved in 30 mL deionized water and thermostated at 40 °C; 0.5 mL of 0.2 M NaOH are slowly added under vigorous mixing until complete dissolution; finally, the pH is buffered to 8.0;

- *preparation of radical initiator*: 5.4441 g of 4,4'-azobis(2-cyanovaleric) acid are dissolved in 30 mL degasified deionized water and thermostated at 30 °C in the vacuum oven for degasification;
- *making-up the starting reaction mass*: the co-monomer M_2 and initiator solutions are added in the reaction vessel, at 40 °C, under mixing and adjusted to pH 8.0;
- *adding of co-monomer M_1* : the adding procedure depend on the expected enchainment fashion ; if the formation of block copolymer sections is wanted, the co-monomer M_1 and inhibitor emulsified mixture is quickly submerged in the starting reaction mass, under vigorous mixing;
- *copolymerization completion* : is accomplished through raising and maintaining the temperature at 95 °C for 15 minutes;
- *post-processing of the reaction mass*: after the reaction time is up, the reaction mass is cooled and kept to 60 °C for 10 minutes, under continuous stirring; after that, the reaction mass is passed into another vessel and cooled to the room temperature under mixing; finally, the reaction mass is degasified;
- *preparation of a product sample for subsequent analyses*: an aliquot of the resulting emulsion is precipitated with acetone and the precipitate is washed with ethylic ether, dried in the vacuum oven and comminuted in a ball mill; the resulting powder is conditioned in the oven and the desiccator, in order to be subjected to FT-IR spectrophotometric analysis, in anhydrous KBr pellet.

RESULTS AND DISCUSSIONS

The FT-IR spectra of the synthesis product is given in Figure 3. The peak from 906.54 cm^{-1} within the 810 - 950 cm^{-1} absorption band confirms the presence of free oxirane groups on the oligomer chain (according to [7], pp. 205-215). The absorption bands between 1300 - 1420 cm^{-1} and 2800 - 2900 cm^{-1} confirm the presence of methylen and methynic groups, respectively, implied in carbocatenary bonds (according to [7], pp. 261-296). The peak at 1581 cm^{-1} indicates the presence of free carboxyl groups while the presence of anhydride rings is confirmed by the 1100 - 1150 absorption band. On the whole, the FT-IR spectrum confirms the expected structure of the oxirane-pendant-groups oligomer: free oxirane groups and enchainned anhydride and maleic acid units as well.

The tanning potential of the synthesis product was ascertained by the following tests: (1) atelocollagen solutions were irreversibly precipitated when reacted with the oxirane copolymer and (2) when reacted with untanned and weakly chromed hide powder, the synthesized oligomer is completely exhausted from the reaction liquor. Since the reactive copolymer was obtained in small amounts, tests on leather samples could not be carried out.

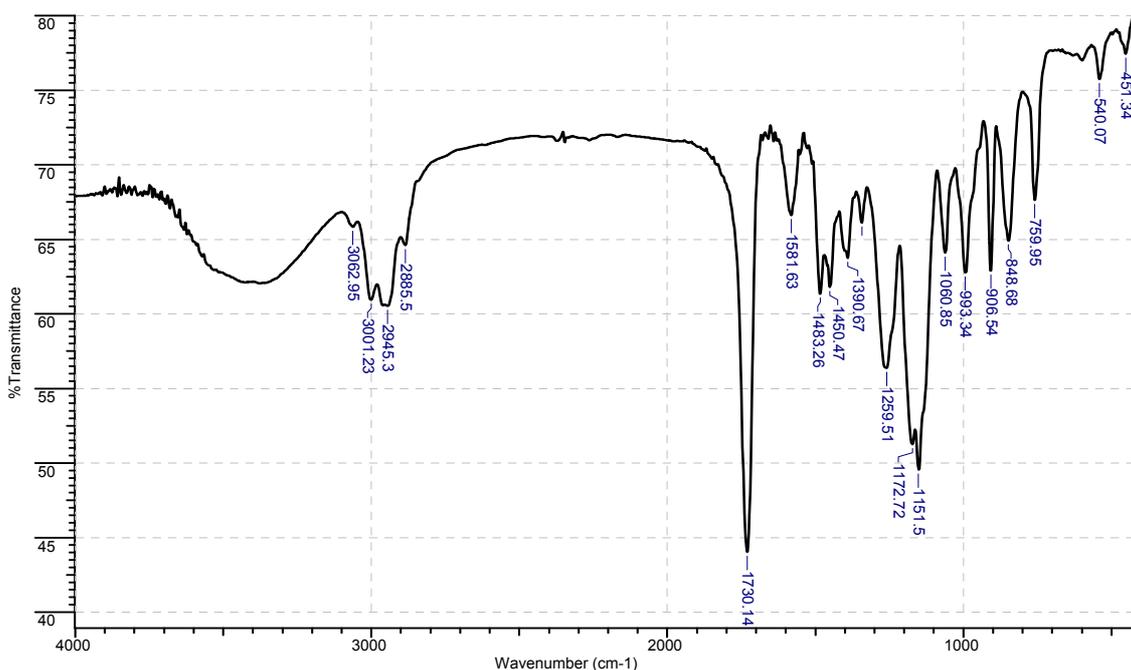


Figure 3. The FT-IR spectra of the copolymerization product

CONCLUSIONS

The synthesis pathway is straightforward but strongly dependent on the working procedure. The obtained product meets the designed characteristics, both as it concerns the chemical structure and the expected functionality as a syntan.

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