European Polymer Journal 46 (2010) 1316–1327

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

A novel route for synthesizing esters and polyesters from the Diels–Alder adduct of levopimaric acid and acrylic acid

Fanica Mustata *, Ioan Bicu

Petru Poni Institute of Macromolecular Chemistry, Romanian Academy of Sciences, Aleea Grigore Ghica Voda 41 A, RO-700487 Iasi, Romania

ARTICLE INFO

Article history:
Received 26 November 2009
Received in revised form 1 March 2010
Accepted 15 March 2010
Available online 19 March 2010

Keywords:
Levopimaric acid
Diels–Alder adduct
Polyesters
Thermal properties
Dielectric properties

ABSTRACT

A novel route for the esterification of the Diels–Alder adduct between abietic acid, in its isomer form of levopimaric acid, and acrylic acid was established. The high purity Diels–Alder adduct was prepared starting from rosin acids. When the adduct was subjected to a condensation reaction in the presence of a cyclic carbonate ester and of an efficient amine catalyst, hydroxyalkyl esters were obtained. The corresponding linear polyesters were synthesized by the advanced polycondensation of the above intermediates at high temperature, under vacuum, and in the presence of some adequate polyesterification catalysts. In the work 1,3-dioxolan-2-one as cyclic carbonate ester, triethylamine as esterification catalyst, and toluene-4-sulfonic acid monohydrate or tetrabutyl titanate as polycondensation catalysts, were preferred for exemplifications. The polyesters were soluble in dimethylacetamide, trichloromethane, tetrahydrofuran, 1,1,2,2-tetrachloroethane, or 1,4-dioxane. The thermal and electric studies showed that the polymers were substances with good thermal stability and high dielectric properties.

1. Introduction

Abietic acid, the major constituent of natural rosin acids, and its adducts with maleic anhydride, maleic acid, fumaric acid or acrylic acid, being low-molecular-weight substances, are quite unsuitable for practical applications. Things are quite different in the case of the esters of abietic acid, or of the polyesters derived from its Diels–Alder adducts. These would have higher melting points, increased hardnesses, reduced brittlenesses, better film-forming and wetting abilities, and increased thermal, oxidation and ultraviolet stabilities. That is why in the last decades a special attention has been given to the development of such high performing abietic acid-based non-polymer, or polymer, products.

The esters of abietic acid (rosin acids) interested, and still interest, because they found innumerable applications as tackifiers for rubber [1,2] and pressure-sensitive adhesives [3–16], as binder for toners [17], as stabilizers in the latex compositions [18], as film-forming materials for coating and delayed release of drugs [5,19–21], as biodegradable and biocompatible materials [22], and even as cream base in cosmetics [23]. The specialty literature offers not a few data attesting the fact that the rosin acid esters with the most different alcohols are non-toxic and non-carcinogen substances [24]. This finding justifies the use of these esters as cosmetic ingredients or even as food additives permitted for direct addition to food for human consumption [25].

It is well known that the esterification of abietic acid is difficult because its molecule is very large in comparison with the polyol molecules and because the carboxylic group is one tertiary and hindered. As such, the esterification of abietic acid with the monohydric and polyhydric alcohols can only be carried out at high temperatures (180–290 °C) and prolonged reaction durations, of 10–20 h [15,17,22,26–29], and even 40 h [30]. Therefore, the condensation reaction seems to be an energy-intensive one. Intending to overcome this drawback, the reaction between alkylhalides and alkaline salts of abietic acid was proposed as a cheaper alternative [31,32]. But, this time,

* Corresponding author. Tel.: +40 232 217454; fax: +40 232 211299.
E-mail address: fmustata@icmpp.ro (F. Mustata).

0014-3057/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2010.03.011

it appeared the necessity to find the solvents for the alkaline soaps, so that the condensation reactions to take place readily in homogeneous media. Other researches showed that the reaction between the tertiary amine salts of carboxylic acids and the polyalkylhalides constitutes a convenient route for the preparation of esters of some hindered acids such as rosin acids, because it is one facile and non-energy-intensive [33–36]. Another time, Halbrook et al. showed that rosin acids can react rapidly with olefin 1,2-epoxides to give mono and diesters [1].

As regards the polyesterification of the Diels–Alder adducts of levopimaric acid with acrylic acid, acrylonitrile, maleic anhydride, or fumaric acid with the diols or polyols, the literature cites some similar, or even heavier, reaction conditions [26,27,37,38]. Another interesting route for the preparation of such polyesters consists of the condensation of the Diels–Alder adduct diacid chlorides with the diols in the presence of an acid acceptor [39]. In spite of the heavier synthesis conditions, the polyesters, in comparison with the esters, prove to be superior with respect to their level of performance. Therefore, their end-uses are quite different from each other, too. The polyesters were used as metal anti-corrosive protecting coatings [20,40,41], basic ingredients for lithographic inks [42], polymer pigment dispersants in paints and inks [26,43], macromolecular prodrugs [44], surfactants in cosmetics [45], adhesives [38], biodegradable and biocompatible materials [46], biomaterials for enteric coatings and delayed release of drugs [47–49].

It must also be mentioned that in the recent years rosin acid derivatives, besides the attention received in polymer synthesis, have also been employed as effective epoxy curing agents [50–56].

The aim of this work is to continue the investigations regarding the opportunities of using the Diels–Alder adducts of abietic acid as monomers for polymer synthesis. More precisely, the article presents a novel, unconventional, route for synthesis of esters and polyesters, supposing the condensation of the Diels–Alder adduct of levopimaric acid with acrylic acid (LPAA) with 1,3-dioxolan-2-one (ethylene carbonate, EC), in the presence of a trialkylamine, as a hydroxyethylation catalyst, and of a sulfonic type catalyst (4-toluenesulfonic acid monohydrate, TSA), or of a titanium type catalyst (tetrabutyl titanate, TBT), as polycondensation catalysts. It must be mentioned here that, so far, there have been published some reports regarding the use of EC along with some aromatic, or aliphatic, diacids in the synthesis of the polyesters [57–62], but there were no reports about the synthesis of the esters and polyesters using the Diels–Alder adduct between levopimaric acid and acrylic acid as a diacid. That is why we report now the synthesis and characterization of the esters and polyesters resulting from the reaction between LPAA and EC.

2. Experimental

2.1. Materials

Rosin acids and LPAA were prepared, separated, and purified as described in Refs. [39,63]. Acrylic acid (AA, Aldrich, 99%), EC (Fluka, 99%), TSA (Aldrich, 98%), triethylamine (TEA, Aldrich, 99%), TBT (Aldrich, 97%) were used as received. The organic solvents were analytical grade.

2.2. Monomer synthesis

2.2.1. Synthesis of the hydroxyethyl esters by the reaction between LPAA and EC

It is known that, the proportion between the alkylene carbonate and the diacid in a condensation reaction exerts a great influence upon the nature and the constitution of the reaction product. Indeed, the condensation reaction between EC and LPAA, carried out in the presence, or in the absence, of a specific catalyst, can end in either a monohydroxyethyl ester (MHE) or a dihydroxyethyl ester (DHE), depending on the molar ratios between the two reactants. It must be also mentioned that TEA was chosen as catalyst owing to its recognized high reactivity and specificity [62].

2.2.1.1. Synthesis of MHE. In a flask fitted with a thermometer, a stirrer, a nitrogen inlet, and a take-off for N_2 and the volatile products were placed 52.8 g (0.6 mol) of EC, 225.0 g (0.6 mol) of LPAA, and 2.9 ml (2.1 g, 0.75 wt%, referred to the weight of the reactants) of TEA. The mixture was heated under an oxygen-free nitrogen atmosphere, with the flask places in an oil bath heated at 175 °C. Stirring was commenced when the reaction mixture had melted. During the next 25 min, the temperature raised at 155 °C. At this moment, the release of a gas (bubbles in the reaction mass) was observed. This gas was carbon dioxide. Its presence was evidenced by means of a diluted solution of calcium hydroxide. But, a high enough reaction rate was reached only in the 160–165 °C temperature range. The reaction was continued at 165 °C for 45 min, when the molten reaction mixture had cleared, and CO_2 evolution practically stopped. The hydroxyethylation reaction was monitored by following the change in the carbon dioxide evolution rate. The reaction was finished during the next 10 min. At the end of the process, the traces of CO_2 and other gaseous by-products were removed by nitrogen entrainment, resulting 251.0 g of crude product as a yellowish, solid material. The cooled reaction mixture was dissolved in diethyl ether. The removal of unreacted reactants and the catalyst was made by filtration and repeated (twice) washing of the solution with distilled water. The reaction product was separated from the diethyl ether solution by precipitation with petroleum ether (b.p. 28–60 °C) and purified by redissolution into diethyl ether and reprecipitation into petroleum ether. The precipitate was dried in the vacuum oven at 50 °C for 8 h to receive 241.3 g (86.8%) of pure MHE.

When synthesis of MHE was carried out in the absence of the catalyst, similar results were obtained only by raising the reaction temperature and the reaction duration up to 200 °C, and 120 min, respectively. But, this time, the condensation reaction might end in, besides MHE, some low-molecular-weight polyesters having hydroxyl and carboxyl end groups.

2.2.1.2. Synthesis of DHE. Into the reaction vessel 70.5 g (0.8 mol) of EC, 151.0 g (0.4 mol) of LPAA, and 1.7 ml (1.24 g, 0.75 wt%, referred to the weight of the reactants) of TEA were introduced. The reaction mixture was heated under a nitrogen atmosphere, by means of an oil bath heated at 175 °C. Stirring was commenced when the reaction mixture had melted. In the first 25 min of heating the reaction temperature reached the value of 150 °C, at which gaseous CO_2 was evolved. The evolution of carbon dioxide was continuously monitored during the hydroxyethylation reaction. The reaction was continued at 165 °C for 60 min, when the release of carbon dioxide ceased. At the close, the reaction mass was purged (10 min) with N_2 to remove the last traces of CO_2 and to provide 185.0 g of crude product, as a yellowish, highly viscous and sticky, liquid material. DHE was separated from the crude reaction mass and purified in the same manner as MHE. Finally, the bottom humid layer of purified DHE was dried in a vacuum oven at 70 °C for 10 h to yield 182.0 g (82.2%) of purified product.

If DHE was synthesized in the absence of the catalyst, similar results were obtained by raising the reaction temperature up to 195 °C, and prolonging the reaction duration to 170 min. Under such conditions the condensation reaction was not very selective, and DHE was impurified with some oligomers having two hydroxyl end groups.

2.3. Polymer synthesis

The polycondensation reaction may be carried out starting either from the above hydroxyethyl esters (MHE and DHE) or, directly, from the initial raw materials, EC and LPAA. In the following, we will describe the first route. In order to increase the reaction rate, some polycondensation catalysts were introduced into the polymerization system. To this end, we chose TSA and TBT as reference catalysts, because the two were recognized as very efficient in the polyesterification reactions [32,57,64–68].

2.3.1. Synthesis of the polyester by the polycondensation of MHE in the presence of TSA (PES-1)

A 0.5-L capacity glass vessel provided with a thermometer, a mechanical stirrer, an ascendant condenser, a N_2 inlet, and a thermostatically controlled heating mantle, was charged with MHE (173 g, 0.4 mol) under nitrogen flow, and heated with stirring up to 125 °C over a period of 15 min for complete melting of the polymer precursor. TSA (0.5 g, 0.3 wt%) was added, and heating with stirring continued, under a nitrogen blanket, at 150 °C for other 45 min. After TSA was added, the reaction mass changed the initial yellowish color into one red-lilac that proved the formation of a catalytic complex between TSA and MHE. In the same time, the formation of water was observed. The preservation of water in system in this polycondensation stage was desired because it exerted a beneficial role on the homogenization of the increasing molecular weights of the polymer. Afterwards, the ascendant condenser was replaced with a descendent condenser fitted with a cold trap. Nitrogen was purged for a short time and an oil vacuum pump was connected to the trap. A vacuum, on the increase from 3 kPa to 200 Pa, was applied slowly over a period of time of about 20 min to avoid the excessive foaming, and even the entrainment of the oligomers. Under these reaction conditions, the polycondensation continued at 175 °C for 90 min. A significant amount (4.5 ml) of condensation water was collected in the trap. In its last part, the polycondensation reaction continued at 185–245 °C, under a vacuum of 4 Pa, for 5 h. Throughout all this time the melted reaction mass became harder and harder to stir, as a result of the increase of the viscosity. At the end, the temperature was raised for a short time up to 240 °C, the vacuum was replaced with nitrogen, and the molten polymer discharged into a porcelain capsule. The yield was 163.3 g (94.4%) of crude yellowish polymer and 5.7 ml of condensation water. Of course, the amount of water collected in the trap was lower than that expected, due to its unavoidable evaporization under the high and prolonged vacuum. The polyester was ground in a mill, washed with methanol, and dried for 8 h, at 50°, in a vacuum oven, to give 159.5 g (92.2%) of purified polymer.

Similar results were obtained when PES-1 was synthesized by a continuous process, starting directly from EC (35.2 g), LPAA (151.0 g), and TSA as catalyst. This time, 155.0 g of purified polymer was obtained, so that the general transformation yield was found to be 83.2%.

The polymerization of MHE was also repeated in the presence of TBT as polycondensation catalyst (Ti added at 140 ppm, referred to the weight of the MHE), but the polyester had a color somewhat darker as compared with the polymer prepared in presence of TSA. The yields were 164.9 g (95.3%) of crude polyester, and 158.2 g (91.4%) of purified product.

2.3.2. Synthesis of the polyester by the polycondensation of DHE in the presence of TBT (PES-2)

On the whole, the technique and the apparatus were the same as above, except the ascendant condenser which was replaced from the beginning with a descendent one. An amount of 187.0 g (0.4 mol) of DHE was heated, under stirring and a N_2 stream, up to 70°. TBT (0.2 g, Ti addition 150 ppm) was fed into the system as a diluted (10%, w/v) solution in trichloromethane. After the removal of the solvent, the reaction mass changed the initial yellowish color into an orange-red one. The four stages of heating, at 125, 150, 150–175, and at 185–245 °C, as well as the corresponding vacuum levels and reaction durations were kept as when MHE was polycondensed in presence of TSA. Finally, 160.8 g (86.0%) of crude product and 26.4 ml of condensation ethylene glycol were obtained. The crude polyester was processed by milling, washing with methyl alcohol and drying in a vacuum oven, to give 158.0 g (84.5%) of purified polymer.

When the polycondensation of DHE was repeated in the presence of TSA as catalyst, the reaction duration of the last polycondensation phase, that at 185–245 °C, must be prolonged up to 10 h, and the addition of the catalyst must be raised up to 0.5%, to get an important increase of the molecular weight, comparable with that generated by TBT. But, even under these reaction conditions the resulting polymer showed a light (yellow) color, and a reaction yield of 157.8 g (84.4%) of crude polyester.

When the polyester was synthesized by an uninterrupted process, starting from EC (70.5 g, 0.8 mol), LPAA (151.0 g, 0.4 mol), TEA (0.75% addition, referred to the weight of the reactants), and TBT (0.2 g, 0.1% referred to the weight of the reaction mass measured at the end of the first condensation stage), the duration of the hydroxyethylation stage (150–165 °C) was 85 min, the total duration of the polycondensation stage (165–245 °C) was 7 h, and the reaction yield was 159.5 g (72.0%) of crude PES-2, or 156.3 g (70.6%) of purified polymer.

2.4. Measurements

Acid number (a.n.) was determined with 0.1N aqueous KOH in the presence of phenolphthalein with acetone, or an 80/20 mixture by weight of pyridine and trichloromethane, as solvents, as the monomers or the polymers were analyzed. The hydroxyl number (h.n.) was determined by the conventional acetic anhydride/pyridine method, according to Refs. [69,70]. Carbon and hydrogen of the compounds were determined by the Pregl method. The melting temperatures were measured by means of a microscope with a heated plate and verified by DSC. Density measurements were performed at 20 °C with a pycnometer. The inherent viscosity was measured viscosimetrically at 25 °C upon the polymer solutions of 0.5% (w/v) concentration in trichloromethane as a solvent, and calculated by using the relation $\eta_{inh} = \ln(t/t_0)/C$, where t and t_0 are the flow times of the polymer solution and solvent, respectively, and C is the polymer concentration expressed in g dl^{-1}. The molecular weights and the polydispersities were determined by gel permeation chromatography (GPC) with a Polymer Laboratories instrument equipped with a PL-EMD 950 evaporative mass detector, and with trichloromethane as solvent. The molecular weights were also determined from the a.n. and h.n. data by using the relation $M_n = 112{,}200/(\text{a.n.} + \text{h.n.})$, according to Ref. [70]. Fourier transform infrared spectra were recorded on a Bio-Rad spectrophotometer, with KBr pellets. ^{1}H NMR analyses were performed with an Avance DRX 400 (Bruker) instrument at 400 MHz. The spectra were referenced to internal tetramethylsilane. Samples were dissolved in $CDCl_3$. Differential scanning calorimetry (DSC) measurements were performed using a 912 DSC Du Pont Instruments apparatus. Thermogravimetric analysis (TGA) was carried out by means of a NETZSCH STA 449 F1 thermal analyzer in nitrogen at a heating rate of 10 °C/min. The dielectric measurements were performed using a NOVOCONTROL CONCEPT 40 dielectric spectrometer. Samples in a form of a thin flat disc were placed between two opposing metallic discs acting as electrodes, and analyzed at room temperature within the frequency range from 1 Hz to 1000 kHz. The determined dielectric parameters were the dielectric constant (relative permittivity) and the dielectric loss tangent (tan δ).

3. Results and discussion

3.1. Synthesis of the monomers

Two monomers, the hydroxyethyl esters of the Diels–Alder adduct of LPA with AA (MHE and DHE) were firstly synthesized by the condensation of LPAA with EC in presence of a very efficient catalyst (TEA) (Scheme 1).

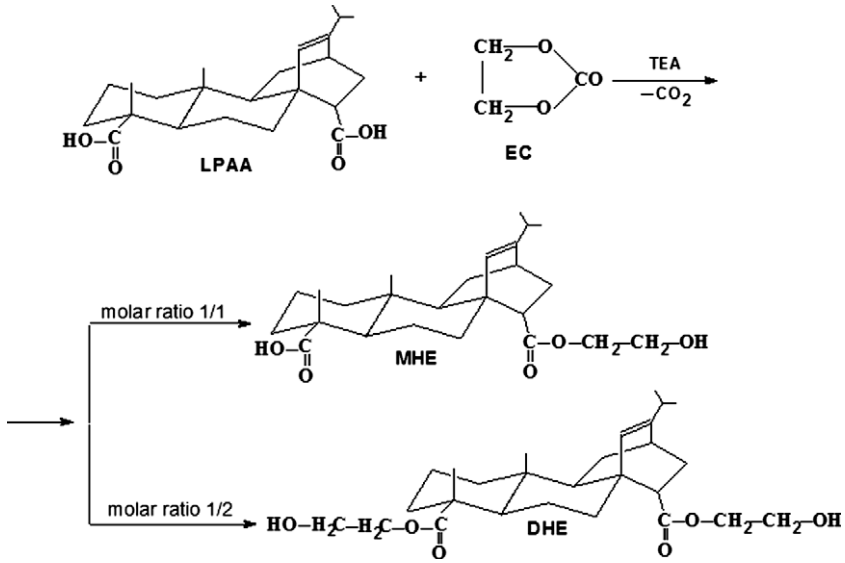
Some specifications are noted here in the connection with the hydroxyethylation procedure. As a rule, the condensation hydroxyethylation of the diacids has been carried out by the direct reaction with the diols, but this route has had some disadvantages, as follows:

- necessitates a long reaction time and a great quantity of thermal energy,
- necessitates an inert solvent to facilitate the homogenization of the reaction mass,
- necessitates a great excess of diol (molar ratios of up to 5:1 were reported) to increase the reaction rate and to shift the reaction equilibrium to the right,
- the removal of the condensation water constitutes a difficult problem, and so on.

All these disadvantages of the prior method were overcome when LPAA was hydroxyethylated by the condensation with EC. The use of ethylene carbonate in the esterification reaction is advantageous because it melts at low temperatures, is chemically stable up to high temperatures and, as such, behaves as a pseudo-liquid substance. In this last state, it is compatible with LPAA, and exhibit a good ability to dissolve both the initial and final reaction products. Under these conditions:

- the condensation duration was shortened to 45–60 min,
- the time necessary for complete homogenization of the reaction mass was considerably reduced, up to 10 min,
- the condensation temperature was lowered to 150-160 °C,
- the molar ratios between the reactants were strictly kept at 1:1, or 2:1, as the achievement of MHE, or DHE, was pursued,
- the evolution of carbon dioxide from the reaction mass not only was very facile and fast, but also provided some beneficial effects as the promotion of the mixing and the formation of an inert blanket in the reaction vessel,
- the preparation of the hydroxyesters was considered finished when CO_2 evolution ceased.

We found that LPAA and EC react readily in the presence of an efficient catalyst, such as TEA, to give the hydroxyethyl esters of LPAA, and even some oligomers, if the reaction temperature and/or the reaction duration surpassed 160–165 °C, or 60 min, respectively. Experimentally, we also found that the optimal catalyst concentration was of 0.75 wt%, based on the amount of the reactants. The high yields after the purification (of 96.2% in the case of MHE and 98.4% in the case of DHE, Table 1) prove that the reaction between LPAA an EC is very effective, and that in syntheses do not form oligomers. The observation is also upheld by the values for c.c. and h.c. (Table 1), found to be very close to the calculated ones. So, EC, as the simplest and the most reactive component of the cyclic carbonate ester group, proves to be a valuable reagent in the transformation of the acrylated levopimaric acid into its hydroxyalkyl monomeric esters.



Scheme 1. Synthesis of MHE and DHE.

Table 1
Physicochemical characterization data of MHE and DHE.

Characteristic	MHE	DHE
State	Solid	Liquid
Conversion (%)[a]	86.8	82.2
Density (g cm^{-1})	1.146	1.137
Melting point (°C)	38.3	−4.5
a.n. (mg KOH g^{-1})[b]	129.5 (134.0)	_
h.n. (mg KOH g^{-1})[b]	130.9 (133.9)	237.8 (242.1)
Elemental analysis: C (%)[b]	72.12 (71.77)	69.81 (70.13)
Elemental analysis: H (%)[b]	8.97 (9.09)	8.89 (9.09)
Molecular weight, M_n[b,c]	440 (418)	484 (462)
Color	Yellowish	Yellowish

[a] Determined from the weight of the purified products referred to the weight of reactants.
[b] Calculated values are in parentheses.
[c] Determined by the vapor pressure lowering method (trichloromethane, 45 °C, and benzil as a standard).

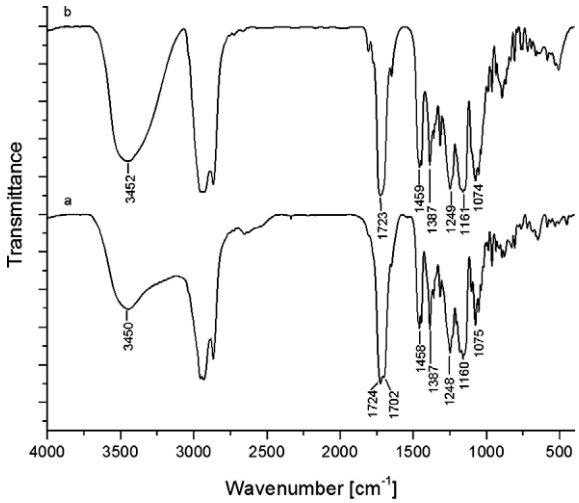


Fig. 1. IR spectra of (a) MHE and (b) DHE.

The purified MHE is a yellowish solid, whereas DHE is a very tacky and viscous, yellowish liquid. Both the hydroxy-esters are soluble in the common organic solvents apart from n-hexane, cyclohexane, and petroleum ether. Their main physicochemical characterization data are presented in Table 1.

As shown in Scheme 1, the products resulting from the condensation of LPAA with EC have a carboxyl group and a hydroxyethyl group (MHE), or two hydroxyethyl groups (DHE). The transformation of LPAA into hydroxyethyl esters by reacting with EC, is evidenced by both the IR and ^{1}H NMR spectral analysis data (Figs. 1 and 2), and the physicochemical characterization data of the reaction products (Table 1). Thus, in the IR spectrum of MHE [Fig. 1(a)] the formation of the hydroxyethyl group, and of the ester linkage, is evidenced by the existence of the absorption bands at 3450 cm^{-1} [(OH)] and at 1724 cm^{-1} [(C=O) in COO ester group], respectively. The presence of the remaining untransformed carboxyl groups in the structure of MHE is reflected by the existence of the band at 1702 cm^{-1} [(C=O) in COOH]. The C—O stretching vibration in esters shows two intense absorptions at 1249 and 1160 cm^{-1}. In the spectrum of DHE [Fig. 1(b)], the formation of the bishydroxy ester is shown by the disappearance of the band characteristic of COOH groups (at 1702 cm^{-1}) and by the increase in intensity of the band at 3450 cm^{-1}, corresponding to the two end OH groups. The presence of the bands at 1459 cm^{-1} [$(CH_3)_{asim}$ in isopropyl group] and at 1385 cm^{-1} [$(CH_3)_{sim}$ in isopropyl group] in the two spectra proves the existence in their chemical structure of the hydrophenanthrene moieties, coming from the starting levopimaric (abietic) acid.

The aforementioned ascertainments remain valid when the ^{1}H NMR spectra (Fig. 2) have been examined. Thus, in these spectra, the formation of the ester linkage and of

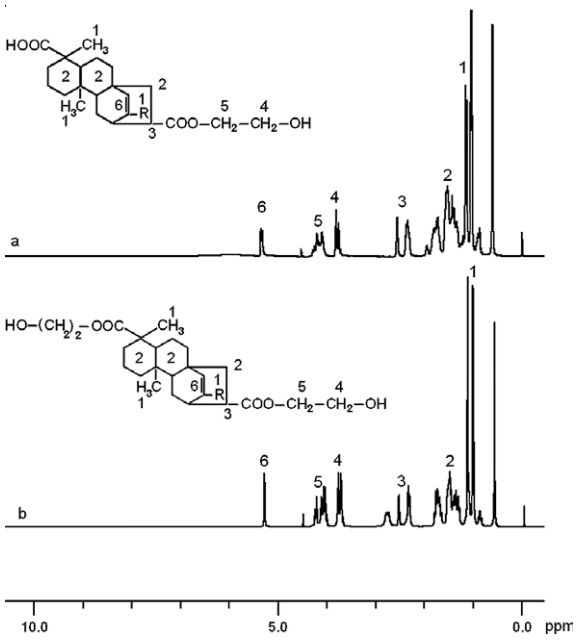


Fig. 2. ^{1}H NMR spectra of (a) MHE and (b) DHE.

the hydroxyethyl groups is reflected by the appearance of the bands in the chemical-shift ranges 4.0–4.35, 3.7–3.85, and 2.3–2.65 ppm, which can be ascribed to the methylene groups of the glycol ester linkages [—*CH*$_2$—O—(C=O)—], the methylene groups adjacent to the hydroxyl groups from the hydroxyethyl rests, and to the methine groups belonging to LPAA acid which are adjacent to the ester linkage [*CH*—C=O)—O—], respectively. The signals in the complex series of peaks in the range from 0.85 to 2.5 ppm can be assigned to the methyl, methylene, and methine groups from the hydrophenanthrene moiety. These partly overlap, in the field 2.3–2.5 ppm, with methine groups of LPAA adjacent to the ester linkage. The signals in the chemical-shift range of 5.32–5.36 ppm are due to the vinyl protons in the hydrophenanthrene moiety. The signals as a quadruplet centered at 3.45 ppm in the spectrum of MHE [Fig. 2(a)] and the signals as a doublet centered at 2.85 ppm in the spectrum of DHE [Fig. 2(b)] can be attributed to the terminal hydroxylic protons. In the spectrum of MHE, surprisingly, the signal corresponding to the carboxyl group is not present. This is probably because $CDCl_3$, although a good solvent for MHE, is not advisable to determine the chemical-shift values characteristic of carboxylic protons. But, the presence of carboxylic group and of the ester group in structure of MHE, and of the ester groups in structure of DHE, is fully evidenced by the ^{13}C-NMR spectral data (Fig. 3). Thus, in the spectrum of MHE [Fig. 3(a)] the resonance signal at 185.4 ppm is characteristic of carboxylic group, and the signal at 175.3 ppm is characteristic of ester group. In the spectrum of DHE [Fig. 3(b)] the resonance signal characteristic of carboxylic group, as expected, disappeared and the signals characteristic of ester groups are present at 175.6 and 179.2 ppm.

3.2. Synthesis of the polymers

In the preparation of the polyesters from LPAA and EC the polycondensation reaction was carried out in two separate stages, although the process could have been operated by an uninterrupted procedure, too. In both cases the polyesters were prepared by reacting LPAA and EC to produce a hydroxyethyl ester, MHE or DHE, mixed or not with its oligomers as an uninterrupted or a discontinuous procedure was approached, and by subjecting the resulting monomer to a condensation polymerization at elevated temperature, under reduced pressure, and in the presence of a catalyst. The polycondensation reaction was performed by using amounts very closed to the stoichiometric, and the polycondensation temperature was constantly kept below 245 °C to prevent the undesired reaction of unbinding of the Diels–Alder adduct between LPA and AA. Ethylene glycol or water, upon occasion, was removed in the beginning by nitrogen entrainment, and later under a good vacuum of up to 4 Pa. The length of heating time, the reaction temperature, and the vacuum intensity were the main parameters which determined the magnitude of the molecular weight of the resultant polyester. The catalysts used in the present research were TSA and TBT. Antimony trioxide, calcium nitrate, zinc acetate, imidazole, and triphenylphosphine were also experimented, but the results were poor and the catalysts were counted as unsatisfactory.

Some specifications are noted here in connection with the polymerization procedure. Because MHE and DHE had low melting temperatures, in both cases the polycondensation in bulk was preferred, intending to obtain polymers having molecular weights as high as possible. So, after a short period of heating a good stirring of the reaction mass was ensured. Thereafter, when TSA catalyst was added, the reaction mixture changed the initial yellowish color into one red-lilac indicating the formation of a catalytic complex between the catalyst and LPAA. Later, as the temperature rose and the polycondensation advanced, it has been observed that the reaction mass became yellowish again. The embrowning of the reaction mass was also remarked when TBT was used as a polycondensation catalyst, but this time the color change was directly proportional to the amount of catalyst, and was irreversible.

The separation and the purification of the whole polymers was carried out by dispersing the crude reaction mass, previously divided as fine grains, into the solvents which dissolved the monomers, the catalyst, and the other low molecular weight by-products, but not the polymer, e.g. methyl alcohol. The greatest yield of purified PES-1 was obtained when the starting intermediates (LPAA and EC), but not MHE, were condensed in the presence of TSA as catalyst. In the case of PES-2, the greatest yield was again registered when the starting intermediates were reacted in an uninterrupted process, but this time in presence of TBT as a catalyst, Table 2. Some other physicochemical characterization data regarding the two polymers are given in the same table.

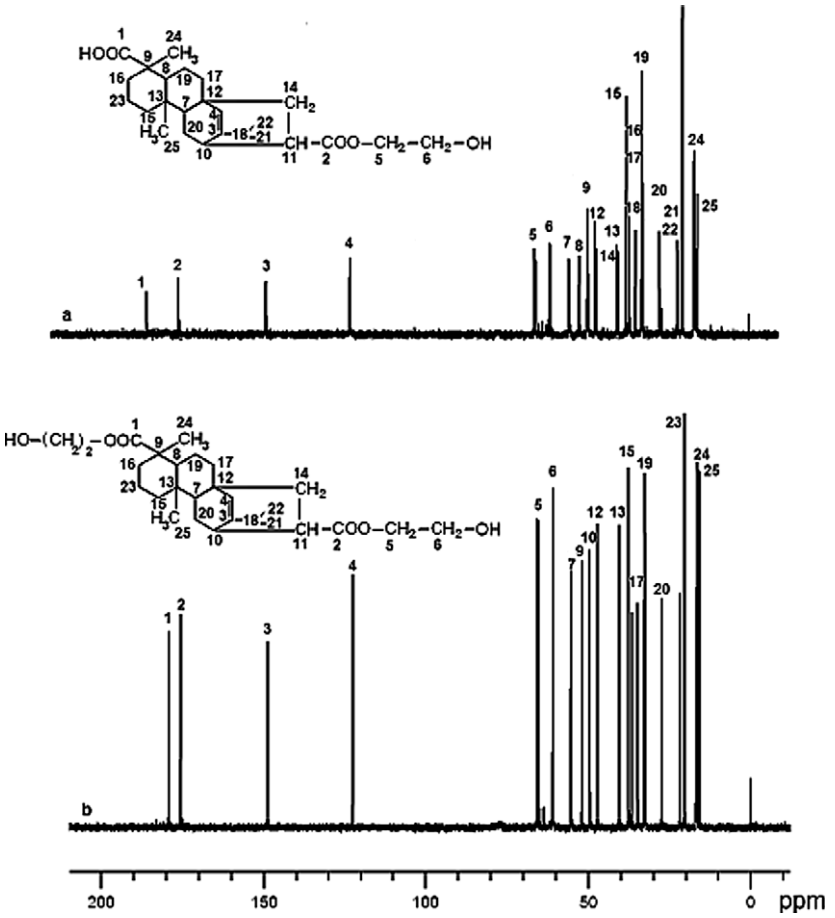


Fig. 3. ^{13}C NMR spectra of (a) MHE and (b) DHE.

Table 2
Physicochemical characterization data of the polyesters (purified products).

Characteristic	PES-1 (MHE + TSA)	PES-2 (DHE + TBT)
Density (g cm^{-1})	1.146	1.137
a.n. (mg KOH g^{-1})	4.86	–
h.n. (mg KOH g^{-1})	4.77	9.15
Inherent viscosity (dl g^{-1})	0.318	0.336
Molecular weight, M_n	11,650[a]	12,260[b]
	11,230 (10,460)[c,d]	12,820 (11,350)[c,d]
	100,50[e]	8880[e]
Polydispersity, M_w/M_n[c]	2.63	1.97
Melting range (°C)	173–178	161–165
Dielectric constant ($_r$)	3.15	3.55
Dielectric loss factor (tan δ)	0.01	0.008
Conversion (%)[f,g]	80.0 (83.2)	69.5 (70.6)
Color	Yellowish	Light brown

[a] Calculated from a.n. and h.n. values.
[b] Calculated from h.n. value.
[c] Gel permeation chromatography method.
[d] Molecular weights of the polymers synthesized by an uninterrupted procedure are in parentheses.
[e] Molecular weights of the polymers synthesized in the presence of the other catalyst.
[f] Determined from the weight of the purified products referred to the weight of reactants.
[g] Yields of the uninterrupted procedures are in parentheses.

3.3. Analysis of polymer chemical structure

The chemical structures proposed for PES-1 and PES-2 are shown in Scheme 2. As shown in the Scheme, the polymers present at the ends of the chains carboxyl groups and hydroxyl groups, or solely hydroxyl groups, as MHE or DHE participated in the polycondensation reaction. However, the back bone structure of the two polymers is not differ-

ent. The carboxyl content, hydroxyl content, melting range, molecular weight data included in Table 2 proves the existence of the polymers shown in Scheme 2. These are in good agreement with the calculated, or the expected values for the proposed structures.

3.4. Spectroscopy

The structures of PES-1 and PES-2 were confirmed by the data of spectral analysis (Figs. 4 and 5), too. But first of all, it should be mentioned that because the IR spectra of the two polyesters do not significantly differ from each other, in Fig. 4 only the FTIR spectrum of PES-1 is presented. The existence of PES-1 is evidenced by the presence in its IR spectrum [Fig. 4(a)] of the characteristic absorption bands located at 1728 cm^{-1} [(C═O) in esters], 1247 and 1137 cm^{-1} [(C—O) in esters], and 1459 [$(CH_3)_{asim}$ in isopropyl group] and 1387 cm^{-1} [$(CH_3)_{sim}$ in isopropyl group of the hydrophenanthrene moiety]. The ^1H NMR spectra (Fig. 5) further support the existence of the polymers in the Scheme 2, by the appearance of the absorbance bands characteristic of the ester linkages. Thus, the methine groups attached to the ester carbonyl group resonate as a complex pattern of absorbance bands centered at 2.50 ppm. The methylene groups attached to the ester oxygen atoms appear as a doublet centered at 4.25 ppm. The peaks at 3.70 ppm can be due to the former terminal CH_2—OH groups in monomer, which by condensation also transform into the methylene groups attached to the ester oxygen atoms. The signals in the chemical-shift range of 5.3–5.5 ppm indicate the presence of vinyl protons, whereas the weak pattern in the chemical-shift range of 6.85–7.25 ppm is due to the pseudoaromatic hydrophenanthrene moiety. The hydroxyl groups in the polymers are represented in the spectra by the weak bands placed at 2.87 ppm.

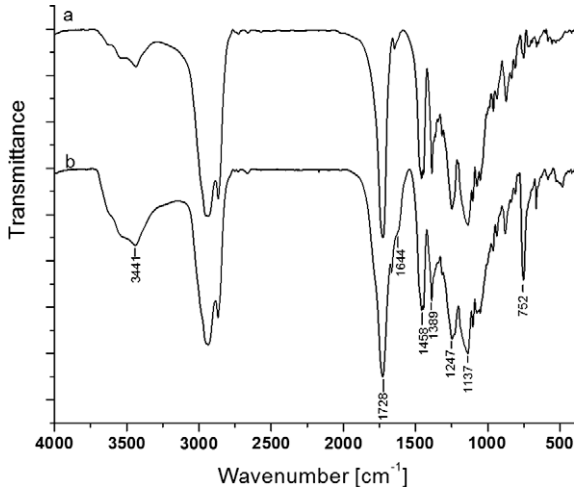
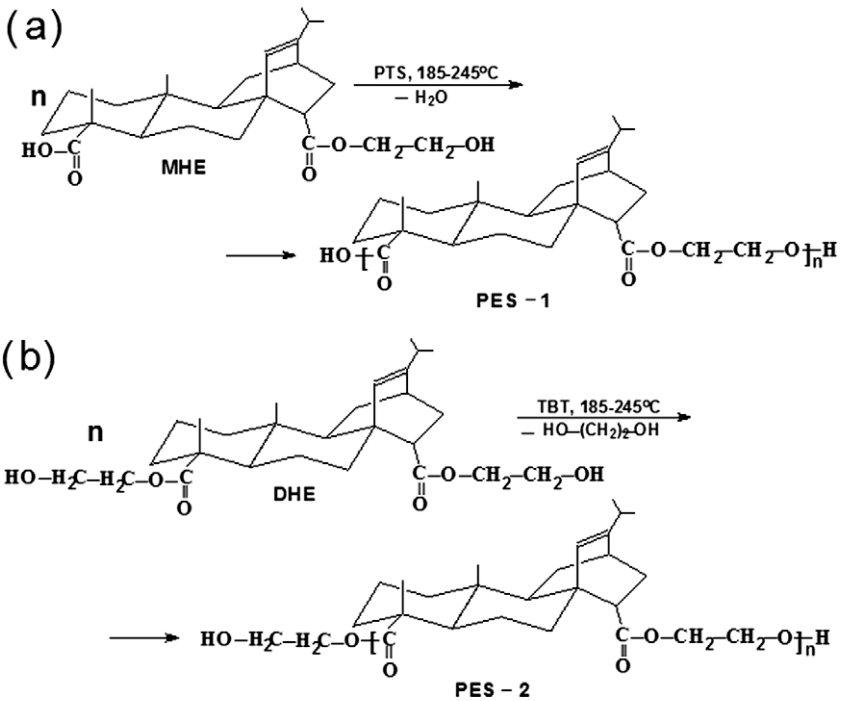


Fig. 4. IR spectra of (a) PES-1 and (b) postpolymerized PES-1.

3.5. Properties of the polymers

The polymers synthesized by the condensation of MHE and DHE, or of the corresponding raw materials (LPAA and EC) are hardly brittle, solid materials having colors varying from yellowish (PES-1, in presence of TSA) to yellow-



Scheme 2. Synthesis of (a) PES-1, and (b) PES-2.

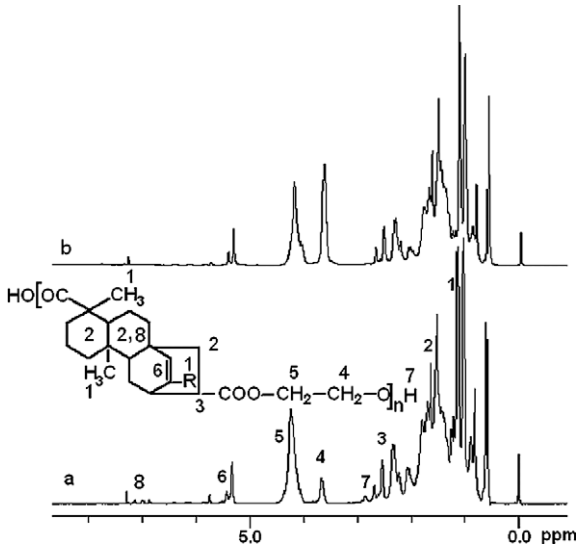


Fig. 5. ^{1}H NMR spectra of (a) PES-1 and (b) PES-2.

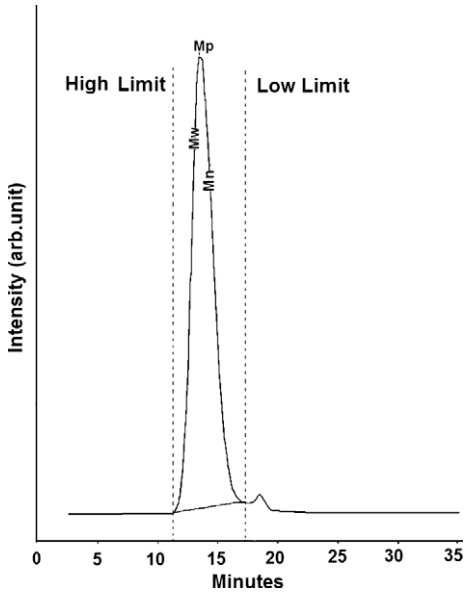


Fig. 6. GPC chromatogram of PES-2 synthesized from DHE in the presence of TBT as a catalyst.

brown (PES-2, in presence of TBT). The molecular weights of the polyesters were measured by end group analysis and gel permeation chromatography (GPC). The GPC curve of PES-2 synthesized from DHE in the presence of TBT as a catalyst is given in Fig. 6. The data regarding the molecular weights of the polyesters are listed in Table 2. On the basis of these molecular weight data we came to the conclusion that the polyesters are medium-molecular-weight polymers. Taking into consideration the molecular weight of the structural unit, 400 g mol^{-1}, we calculated some average degrees of polymerization varying from 26 to 31. The solubilities of the polyesters were tested in different organic solvents at room temperature. All the polymers exhibit good solubility in some polar solvents such as N,N-dimethylformamide, N,N,-dimethylacetamide, tetrahydrofuran, dimethyl sulfoxide, or some chlorinated solvents such as trichloromethane, and 1,1,2,2-tetrachloroethane. Some other characterization data are given in Table 2, too.

As can be seen in Table 2, contrary to expectations, the conversions registered in the uninterrupted processes appear to be greater than the corresponding values registered when the polycondensation was carried out by a discontinuous procedure. The explanation consists of the supplementary purification of the monomers in the middle of the synthesis, in the first case. On the other hand, in the same Table, one can observe that the conversion data regarding PES-2 are somewhat smaller as compared with that characteristic of PES-1, because in this case ethylene glycol, but not water, was evolved from the polycondensation reaction. Another interesting finding concerning the molecular weights refers to the fact that the polymers produced by the polycondensation of MHE in the presence of TSA, and of DHE in the presence of TBT, presented the greatest values. This means that the polycondensation of purified monomers is advantageous from this point of view. Also, when the monomers and the catalysts were inversely combined, not so high as aforementioned values were registered. This denotes that TSA is advisable for the condensation of the monomers having carboxyl and hydroxyl end groups, the reaction being associated with the formation of water as a micromolecular product, whereas TBT is advisable for the condensation of the bishydroxyalkylene compounds, this time the micromolecular compound being a glycol. TSA, as well as TBT, proved to be efficient esterification catalysts, although it was found that the first can also catalyze some side reactions at elevated temperatures (over 200 °C), to give polymers that had somewhat lower molecular weights, as compared, for example, with TBT. It is also true that there are situations in which the side reactions can contribute, contrary to expectations, to the improvement of the performances of the polyesters derived from LPAA and EC. It is the case of the side reactions which took place during the solid-state postpolymerization of PES-1. After the polymer divided into fine grains was heated at 180 °C in an oven under a vacuum of 100–200 Pa for 4 h, the surface of the molten polymer covered with a crust having a somewhat darker color. The polymer in this layer, which in the meantime became insoluble in trichloromethane, was separated from the untransformed polymer by dispersing the complex material in the aforementioned solvent, filtering, and drying. The resulted insoluble fraction was analyzed by FTIR, and the spectrum was presented in Fig. 4(b). By comparing this spectrum with the spectrum of the untransformed polyester [Fig. 4(a)] one can observe that the main modifications consists of the appearance of a strong absorption band, as a shoulder, at 1644 cm^{-1} [(C=C) in aromatics], and of a strong absorption band at 752 cm^{-1} [(CH) in aromatics]. The two bands can be ascribed to the increase in the aromatization of the hydrophenanthrene moiety, as a result of the dehydrogenation side reactions caused by the oxygen in the air in the oven. The increase in the aromatization of the hydrophenanthrene moiety has been also reflected in the ^{1}H NMR spectra of the polyesters (Fig. 5),

by the appearance of the aromatic hydrogen band pattern in the chemical-shift range from 6.85 to 7.25 ppm. By the aromatization of the hydrophenanthrene moiety the chemical structure of the present polyesters became similar to the chemical structure of the polyesters derived from the fully aromatic diacids, and as a consequence the solubility in the common organic solvents, as trichloromethane, diminished, or disappeared. However, the thermally post-treated PES-1 remains soluble in the polar solvents, for example N,N-dimethylacetamide. When the inherent viscosity of the post-treated PES-1 was determined, it was found to be 0.377 dl g^{-1}, slightly greater than the corresponding value characteristic of unmodified PES-1, 0.318 dl g^{-1}, Table 2.

Experimentally we observed that the produced polyesters can be spun in the molten state, but the resulting fibers did not yet exhibit the capability to be cold drawn because of the medium-molecular-weight of the synthesized polymers, and this in turn because of, *inter alia*, the bulkyness of the hydrophenanthrene moiety in the polymer chains.

3.5.1. Thermal properties

The thermal behavior of the polyesters was investigated by DSC and TGA. In Fig. 7 are shown the DSC thermograms, and in Fig. 8 the TGA thermograms of PES-1 and PES-2. Table 3 summarizes some thermal characterization data calculated from DSC and TGA curves. The DSC thermograms in Fig. 7 and the data registered in the first two columns in Table 3 prove the existence of only one well defined glass transition temperature (T_g), varying from 107.4 °C for PES-1 to 118.2 °C for PES-2, and one hardly seen melting temperature (T_m), varying from 181 °C for PES-1 to 168 °C for PES-2. All these findings indicate that each polymer consists of one preponderant amorphous phase. The TGA data included in Table 3 and the TGA thermograms in Fig. 8 show that, on the whole, the polyesters can be considered as fairly thermostable substances. Indeed, if the data regarding the decomposition temperature associated to 10% weight loss (DT_{10}) are considered as criterium for thermal stability, one can see that these fall in the range 370–375 °C. The fast decomposition of the polymer backbone took place at temperatures placed in the range 375–450 °C. The amount of residue after the complete pyrolysis of the polymer sample

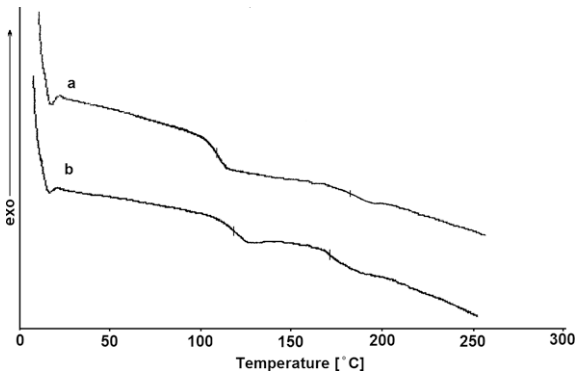


Fig. 7. DSC thermograms of: (a) PES-1 synthesized in the presence of TSA and (b) PES-2 synthesized in the presence of TBT.

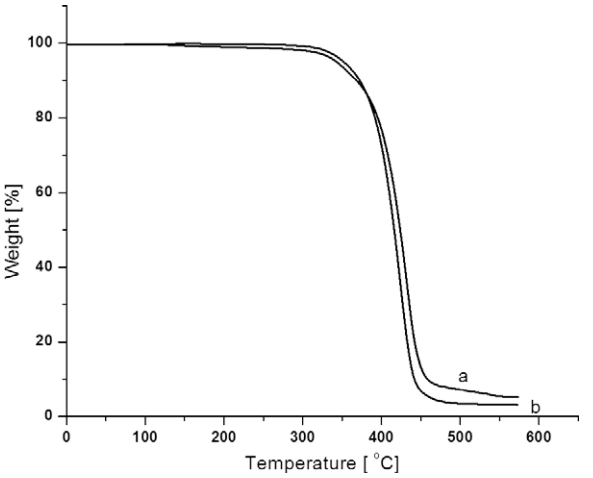


Fig. 8. TGA traces of (a) PES-1, and (b) PES-2.

Table 3
Thermal properties of the synthesized polyesters.

Polymer	T_g (°C)	T_m (°C)	DT_0 (°C)	DT_{10} (°C)	WL_{500} (%)
PES-1	107.4	181	305	370	95
PES-2	118.2	168	315	375	93

DT_0: initial decomposition temperature.
DT_{10}: decomposition temperature associated to 10% weight loss.
WL_{500}: weight loss at 500 °C.

was 5–7%. The increased thermostability of these polyesters can be ascribed to the simultaneous action of some factors as follows: the insertion in the macromolecular chain of the hydrophenanthrene units with a pseudoaromatic character, the disappearance of the more vulnerable conjugated double bonds in the hydrophenanthrene moieties by diene coupling, and the insertion of the acrylic acid segments into their chemical structure. As can be seen in the same Fig. 8, no significant differences exist between the thermal properties of the two polyesters.

3.5.2. Dielectric properties

Dielectric spectroscopy measures the dielectric properties of the polyesters as a function of frequency. Its basic principle consists of the interaction of an external electric field with the electric dipole moment of the sample. Often this interaction is expressed as the relative static permittivity, or the dielectric constant (ε_r), and as the dielectric loss factor, or the loss tangent ($\tan\delta$). With respect to the application of polyesters for electronics, and not only, the change of dielectric properties with frequency is of particular interest. Frequency dependence of ε_r and of $\tan\delta$ of the synthesized polyesters was studied in the frequency range from 1 to 10^6 Hz, at a constant temperature of 25°. Fig. 9 gives the typical results regarding the variation of both the ε_r and $\tan\delta$ with frequency for the two polyesters.

The general finding that comes out from the analysis of the data in Fig. 9 is that in both cases the value of ε_r slightly decreases, and the value of $\tan\delta$ increases, with increasing frequency. The dielectric constant decreases from 3.2 (PES-

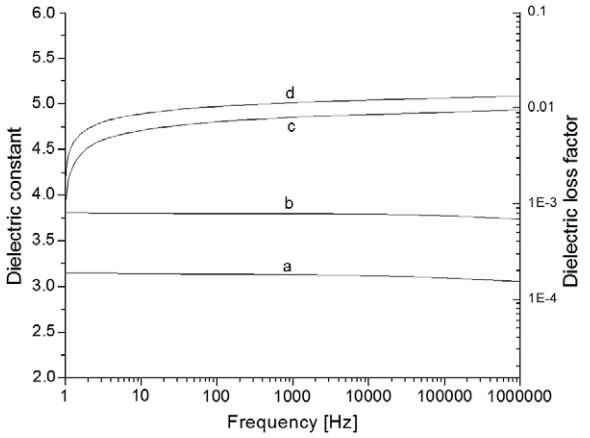


Fig. 9. Frequency dependence of dielectric constant (ε_r) for (a) PES-1 and (b) PES-2, and dielectric loss factor (tan δ) for (c) PES-1 and (d) PES-2, at 25 °C.

1, 1 Hz) to 3.15 (PES-1, 1 MHz), and from 3.6 (PES-2, 1 Hz) to 3.55 (PES-1, 1 MHz). The dielectric loss factor increases from 0.001 (PES-1, 1 Hz) to 0.012 (PES-1, 1 MHz), and from 0.0008 (PES-2, 1 Hz) to 0.0095 (PES-1, 1 MHz). The decrease of ε_r with the increase of frequency is characteristic of the majority of dielectric materials. This tendency can be attributed to the fact that, at high frequencies, the rotational motion of the highly polar molecules of the dielectric polyester is not fast enough to maintain the equilibrium with the electric field and, as a consequence, ε_r slightly decreases with the increase of the frequency. On the other hand, the increase of tan δ with the increase of the frequency, also characteristic of the dielectric materials, denotes that the energy required to align the dipoles in the electric field increases with the increase of frequency.

On the whole, we can assert that the modification of the frequency conditions does not significantly alter the dielectric properties of the synthesized polyesters. Worthy of note are the values for ε_r and tan δ corresponding to the frequency of 60 Hz and the temperature of 25 °C, 3.2 and 0.01, respectively, that were included in Table 2, too. One can observe that these are very near to those characterizing the polyesters of therephthalic acid.

4. Conclusion

Some rosin-based esters and polyesters were synthesized for the first time by reacting the Diels–Alder adduct between levopimaric acid and acrylic acid (LPAA) with 1,3-dioxolan-2-one (EC). EC, in the presence of a catalyst, reacted with the acrylated levopimaric acid (LPAA) to form glycol esters. The esters were used as monomers in polymer synthesis. The polyesterification reaction was also carried out by the direct polycondensation of the starting materials, LPAA and EC. The polyesters were amorphous and medium-molecular-weight polymers, with high melting temperatures, good thermal stability, and high dielectric properties. These were soluble in some organic solvents such as trichloromethane, 1,1,2,2-tetrachloroethane, N,N-dimethylformamide, N,N,-dimethylacetamide, tetrahydrofuran, or dimethyl sulfoxide. The properties of the prepared polyesters make them be potentially applied in the modern electrical and electronic industries, especially for the environmentally friendly green products.

References

[1] Halbrook NJ, Schuller WH, Lawrence RV. Esters of rosin and olefin epoxides. J Am Oil Chem Soc 1968;45:343–4.
[2] Branlard P, Mondiano J. Preparation of polychloroprene for use in adhesives. US Patent 3,872,043; 1975.
[3] Hazen J, Aarts PPM. Polyester tackifier and adhesive composition. US Patent 6,653,398; 2001.
[4] Johnson RW. Acid-modified polyhydric alcohol rosin ester tackifiers and hot melt adhesive compositions containing those tackifiers. US Patent 5,120,781; 1992.
[5] Carrara D. Composition for controlled and sustained transdermal administration. US Patent 6,231,885; 2001.
[6] Sasaki Y, Ercillo J. Pressure-sensitive adhesives based on preferentially tackified immiscible elastomers. US Patent 5,290,842; 1994.
[7] Hemmings P, Wang L. Rosin ester derivative as surfactants, US Patent 5,552,519; 1996.
[8] Rohde WA, Hedrick GW. Esters of rosin acids and glycidyl ethers. J Am Oil Chem Soc 1970;47:3–4.
[9] Puerkner E, Onusseit H. Use of polyester resins as hot-melt adhesives, US Patent 5,518,571; 1996.
[10] Acharya V, Lakshmanan PR. Hot melt adhesive compositions containing rosin esters. US Patent 4,325,853; 1982.
[11] Pfoehler P, Fietzek H. Aqueous polymer dispersions, useful for production of self adhesive tape, etc.-containing acrylic ester copolymer, rosin, polyisocyanate, emulsifiers and water. DE Patent 4,007,637; 1991.
[12] Matzinger MD. Method for preparing phenolic rosin resins. US Patent 5,969,071; 1999.
[13] Urbath H, Klein J, Windhoevel UF. Mixture of rosin and wax used in aqueous adhesive dispersion for bonding floor, wall and ceiling coverings. DE Patent 19831000; 1999.
[14] Tanaka Y, Tsunemine N, Konosu O. Rosin containing emulsion for pressure-sensitive adhesive. Eur Patent 0997514; 2000.
[15] Yoshikazu S, Itsuki T. Process for producing phenol-modified rosin ester, phenol-modified rosin ester, and uses thereof. Eur Patent 1113030; 2001.
[16] Heemann M, Gensch I. Use of a resin for producing a hot-melt-type adhesive. US Patent 2003105259; 2003.
[17] Matsumura A, Shigematsu S. Binder for a toner comprising a polyester from rosin or hydrogenated rosin. US Patent 4,981,939; 1991.
[18] Alford JA. Disodium ethoxylated rosin half esters of sulfosuccinic acid as foam stabilizers for latices and compositions containing same. US Patent 4,238,380; 1980.
[19] Puranik PK, Dorle AK. Study of abietic acid glycerol derivatives as microencapsulating materials. J Microencapsul 1991;8:247–52.
[20] Pathak YV, Nikore RL, Dorle AK. Study of rosin and rosin esters as coating materials. Int J Pharm 1985;24:351–4.
[21] Sheorey DS, Dorle AK. Release kinetics of drugs from rosin-glycerol ester micro-capsules prepared by solvent evaporation technique. J Microencapsul 1991;8:243–6.
[22] Sahu NH, Mandaogade PM, Deshmukh AM, Meghre VS, Dorle AK. Biodegradation studies of rosin-glycerol ester derivative. J Bioact Compat Polym 1999;14:344–60.
[23] Dhanorkar VT, Gawande RS, Gogte BB, Dorle AK. Development and characterization of rosin-based polymer and its application as a cream base. J Cosmet Sci 2002;53:199–208.
[24] U.S. Environmental Protection Agency (EPA). High Production Volume (HPV) Challenge Program. Robust Summaries Test Plans: Rosin Esters. Internet address: http://www.epa.gov/oppt/chemrtk/rosnstrs/c13552tc.htm.
[25] Food Additives Permeated for Direct Addition to Food for Human Consumption. Internet address: http://www.cfsan.fda.gov/~lrd/fr070822.html.
[26] Jones MF. Novel surfactants. GB Patent 2,155,942; 1985.
[27] Gaudl KW. Acrylated maleic-modified rosin esters and methods of preparing same. US Patent 6,583,263; 2002.
[28] Hoa LTN, Pascault JP, My LT, Son CPN. Unsaturated polyester prepolymer from rosin. Euro Polym Jnl 1993;29(4):491–5.

[29] Symmes EM. Method of producing abietic acid esters of polyglycerol. US Patent 1,696,337; 1928.
[30] Doo WK, Dong KY, Sung HJ. Synthesis and characterization of rosinester modified with p-nonylphenolic resole. J Ind Eng Chem (Korea) 2000;6:256–61.
[31] Johnston AC. Method of producing alkyl esters of abietic acid. US Patent 1,749,482; 1930.
[32] Borglin JN. Heterocyclic-esters of resin acids. US Patent 2,012,622; 1935.
[33] Wagenknecht JH, Baizer MM, Chruma JL. A rapid mild esterification method. Synth Commun 1972;2(4):215–9.
[34] Holmberg K, Hansen B. Methylene diesters of carboxylic acids from dichloromethane. Tetrahedron Lett 1975;16:2303–6.
[35] Arimoto K, Zinkel DF. New esterification method for resin acids. J Am Oil Chem Soc 1982;59:166–8.
[36] Zinkel DF, Arimoto K. Preparation of esters of resin acids, resins, rosins, and derivatives thereof. US Patent 4,405,514; 1983.
[37] Berry D, Schuller US, Lawrence R, Bunk A, Halbrook N. Holt-melt adhesive composition containing glycerol ester of fumaric-modified rosin. US Patent 3,787,342; 1974.
[38] Tsuchida S, Kodama Y. Holt-melt adhesive compositions comprising a partially (fumarized and/or maleinized) disproportionated rosin ester tackifier. US Patent 4,618,640; 1986.
[39] Bicu I, Mustata F. Polymers from a levopimaric acid–acrylonitrile Diels–Alder adduct: synthesis and characterization. J Polym Sci Part A; Polym Chem 2005;43:6308–22.
[40] Atta AM, El Saeed SM, Farag RK. New vinyl ester resins based on rosin for coating applications. React Funct Polym 2006;66: 1596–608.
[41] Atta AM, Nassar IF, Bedawy HM. Unsaturated polyester resins based on rosin maleic anhydride adduct as corrosion protections of steel. React Funct Polym 2007;67:617–26.
[42] Burke RE, Sprull JG. Flushing vehicles for preparing flushed organic pigments and method for preparing the same. US Patent 5,420,229; 1995.
[43] Bender A, Giencke A. Modified natural-resin acid–aldehyde adducts. US Patent 5,708,078; 1998.
[44] Hussain MA. Unconventional synthesis and characterization of novel abietic acid esters of hydroxypropylcellulose as potential macromolecular prodrugs. J Polym Sci Part A; Polym chem 2008;46:747–52.
[45] Armstrong DP, Lukenbach ER, Verdicchio RJ. Modified rosin esters. US Patent 4,260,550; 1981.
[46] Fulzele SV, Satturwar PM, Dorle AK. Study of the biodegradation and in vivo biocompatibility of novel biomaterials. Eur J Pharm Sci 2003;20:53–61.
[47] Fulzele SV, Satturwar PM, Dorle AK. Study of novel rosin-based biomaterials for pharmaceutical coating. AAPS Pharm Sci Tech 2002;3(4). article 31.
[48] Barabde UV, Fulzele SV, Satturwar PM, Dorle AK, Joshi SB. Film coating and biodegradation studies of new rosin derivative. React Funct Polym 2005;62:241–8.
[49] Mandaogade PM, Satturwar PM, Fulzele SV, Gogte BB, Dorle AK. Rosin derivatives: novel film forming materials for controlled drug delivery. React Funct Polym 2002;50:233–42.
[50] Liu X, Xin W, Zhang J. Rosin-derived imide–diacids as epoxy curing agents for enhanced performance. Bioresour Technol 2010;101: 2520–4.
[51] Atta AM, Mansour R, Abdou MI, El-Sayed AM. Synthesis and characterization of tetra-functional epoxy resins from rosin. J Polym Res 2005;12:127–38.
[52] Mustata F, Bicu I. The effect of some Diels–Alder adducts of resin acids on the process of epoxy resin curing. Polimery 2008;53: 24–30.
[53] Bicu I, Mustata F. Water soluble polymers from Diels–Alder adducts of abietic acid as paper additives. Macromol Mater Eng 2000;280–281:47–53.
[54] Bicu I, Mustata F. Crosslinked polymers from resin acids. Angew Makromol Chem 1996;234:91–102.
[55] Wang H, Liu B, Liu X, Zhang J, Xian M. Synthesis of biobased epoxy and curing Agents using rosin and the study of cure reactions. Green Chem 2008;10:1190–6.
[56] Wang H, Liu X, Liu B, Zhang J, Xian M. Synthesis of rosin-based flexible anhydride-type curing agents and properties of the cured epoxy. Polym Int 2009;58:1435–41.
[57] Ham GE. Process for producing synthetic linear condensation copolyesters using an alkylene carbonate. US Patent 2,870,124; 1959.
[58] Lincoln J. Manufacture of high linear polyesters from refractory aromatic dicarboxylic acids and cyclic glycol carbonates. US Patent 3,009,903; 1961.
[59] Bockmann A, Vernaleken H, Bottenbruch L, Rudolph H, Schnell H. Heterocyclic catalysts for esterification of aromatic dicarboxylic acids with cyclic carbonates of alkylene gylcols. US Patent 3,549,692; 1970.
[60] Wu Y. Esterification process. US Patent 4,266,046; 1981.
[61] Fagerburg DR. Reaction kinetics of the reaction of terephthalic acid and ethylene carbonates. J Appl Polym Sci 1985;30:3617–23.
[62] Thomsen J, Fagerburg DR. Polyesters and their manufacture from acids and glycol carbonates. US Patent 4,594,406; 1986.
[63] Bicu I, Mustata F. Polymers from a levopimaric acid–acrylic acid Diels–Alder adduct: Synthesis and characterization. J Polym Sci Part A; Polym Chem 2007;45:5979–90.
[64] Bajpai UDN, Nivedita. Synthesis of plasticizing polyesters of dimer acid and propane-diol. J Appl Polym Sci 1993;50:693–7.
[65] Behera GC, Ramakrishnan S. Transesterification polycondensation: the role of the catalyst, monomer structure, and polymerization conditions. J Polym Sci Part A; Polym Chem 2004;42:102–11.
[66] Al Ghatta H, Ballico E, Giovannini A. Process for the preparation of polyester resin. US Patent 6,143,837; 2000.
[67] Iwaya Y, Mukai K, Kawanishi M, Nishinohara M. Aliphatic polyesters and method of preparing the same. US Patent 5,504,148; 1996.
[68] Bikirias DN, Achilias DS. Synthesis of poly(alkylene succinate) biodegradable polyesters. I. Mathematical modelling of the esterification reaction. Polymer 2006;47:4851–60.
[69] Kasterina TN, Kalinina LS. Analiza chimica a rasinilor sintetice si a maselor plastice (translation from Russian). Bucuresti: Ed.Technica; 1965.
[70] Sorenson WR, Sweeny F, Campbell TW. Preparative methods of polymer chemistry. 3rd ed. New York: Wiley Interscience; 2001.