

Studies on the synthesis of hydroxyl-terminated isophthalate-based oligoesters via transesterification reaction

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Abstract

A series of isophthalate-based oligoesters was synthesized via the transesterification reaction of dimethyl isophthalate (DI) with various aliphatic diols under different diol(s)/diester molar ratios. The effect of a series of reaction parameters, such as the diols/diester molar ratio, the molar ratio of the diols in the reaction mixture, the species of the diol, the reaction time, the heating procedure, and the species and the amount of the Lewis acid catalyst, on the physical state, the polydispersity, the M_n , the viscosity and the non-volatiles by weight (NVW) of the synthesized oligoesters was studied. A new synthetic procedure for the synthesis of high-solids liquid oligoesters in high yields and high conversions via the transesterification reaction is proposed. The properties of a reference solid oligoester (RefOL) derived from the reaction of DI with the 1,6-hexanediol (HD) (mol ratio DI/HD = 1/1.43), were compared to those of a high-solids liquid oligoester (L-311) prepared from the transesterification of DI with a mixture of HD and 2-methyl-1,3-propanediol (MP) (mol ratio DI/HD/MP = 1/1.50/1.50). The new high-solids liquid oligoester (L-311) presented more enhanced physical properties than its solid counterpart and owing to its improved processability is expected to be a very promising candidate when used as a binder for the preparation of mar-resistant clearcoats or pigmented coatings. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Transesterification; Oligoesters; High-solids resins

1. Introduction

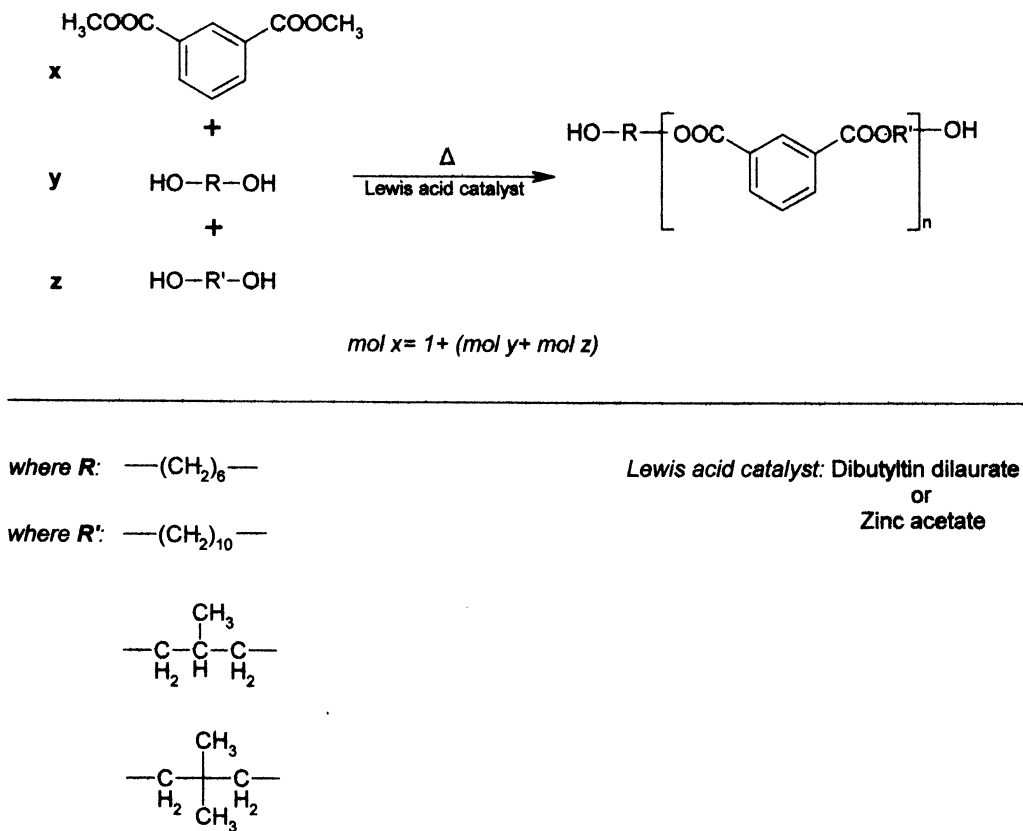
High-solids resins are nowadays of great importance for the coatings and paints industry as a result of the strict limitations imposed worldwide on the use of products with a high level of volatile organic compounds (VOC). One of the most important aims of modern research in the coatings field has to do with the development of new, more environment-friendly chemistries and, at the same time, with the preparation of high-solids resins and, subsequently, coatings of low-VOC. Oligoesters are resins that are widely used by the coatings and paints industry because they combine low production cost with good performance when used as binders in the preparation of coatings. Much effort has been spent for the preparation of high-solids oligoester resins.

The synthesis of a series of high-solids oligoesters prepared via the transesterification reaction of dimethyl

isophthalate (DI) with diols such as 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol (HD) and 1,10-decanediol (DD), under various diol/diester molar ratios, has been reported [1] previously by our group. These solid oligoesters were used as binders in the preparation of low-VOC mar-resistant automotive clearcoats upon crosslinking with a monomeric methylolated melamine-formaldehyde resin “Resimene-747” (hexakis(methoxymethyl)melamine resin, HMMM). A clearcoat derived from an oligoester of the aforementioned series presented an enhanced mar resistance. The oligoester was synthesized from the reaction of DI with HD under a diol/diester molar ratio (R) = 1.43. The mar resistance of all those clearcoats and the identification of different responses of the coatings to marring stress, were investigated using a novel experimental method [2–5], first described and developed by our group. Even though the results with regard to the mar resistance were satisfying, the fact that the aforementioned oligoester was solid severely restricted its potential industrial applications for mar-resistant coatings. Our aim was to synthesize a liquid oligoester, which would combine an enhanced processability and low-VOC, and its corresponding coatings to present comparative or even better physical, chemical and mechanical properties than the above-mentioned clearcoats. Both requirements — if

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Scheme 1.

satisfied — will not only be of academic interest but will also permit substantially more important applications such as the mar-resistant finish to use low-cost oligoester resins (e.g. automotive clearcoats) in the coatings and paints business.

The present work addresses the effect of the various parameters of the transesterification reaction (the diol(s)/diester molar ratio, the molar ratio of the diols in the reaction mixture, the species of the diol, the reaction time, the heating procedure, the species and the amount of the Lewis acid catalyst), on the physical state, the polydispersity (D), the M_n , the viscosity (η) and the non-volatiles by weight (NVW) of the synthesized oligoesters. A series of oligoesters was synthesized in straightforward process via a transesterification reaction of DI, HD and various other aliphatic diols such as 2-methyl-1,3-propanediol (MP), neopentyl glycol (NG) or 1,10-decanediol (DD). The investigation of the effect that the different reaction parameters have on the properties of the synthesized isophthalate-based oligoesters and the optimization of the experimental data resulted in a profound knowledge of how it is possible to obtain high yields of high-solids liquid HO-terminated oligoesters with enhanced processability.

A new synthetic procedure that combines all the optimized experimental data is also proposed and it has been used to accomplish the synthesis of a high-solids liquid isophthalate-based oligoester. Its enhanced physical

properties and subsequent easier processability when compared to those of its solid counterpart will be the subject of future investigation when used as a binder in mar-resistant coatings. In addition, we will also continue our efforts to associate the chemical structure of coatings with their mar resistance because although the physics of the marring has been widely studied, there have been relatively few published theories of how specific chemical structures affect mar resistance [6–8].

2. Experimental

2.1. Characterization methods

FT-IR spectra were obtained from a Nicolet 510P FT-IR spectrometer. ^1H NMR spectra were recorded using a Bruker AC-250 spectrometer at 250 MHz. ^{13}C NMR and ^{13}C DEPT spectra were recorded on a Bruker AC-250 spectrometer at 60 MHz. Modulated differential scanning calorimetry (MDSC) analyses were performed with a DuPont TA 2100 Thermal Analyzer using a high temperature (600°C) cell in N_2 atmosphere at a heating rate of $5^\circ\text{C}/\text{min}$. Gel permeation chromatography (GPC) analyses were carried out with a Hewlett Packard 1050 series Liquid Chromatograph with an HP 1047A differential refractometer as detector. Tetrahydrofuran (THF) was used as a

solvent at a flow rate of 0.9 ml/min through a series of three Phenogel[®] columns (pore size: 10^5 , 10^3 , 10^2 Å) and polystyrene was used for the standardization. Gas chromatography (GC) analyses were performed using a Hewlett-Packard 5809A Gas Chromatograph with a flame ionization detector (FID). 1,4-butanediol was used as internal standard and the silate agent was a mixture of 80/20 v/v of hexamethyldisilazane (HMDS) and *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The viscosities η (cP) of the oligomers were determined using a Brookfield DV-II+ Viscometer, at 25°C and at a spindle rate of 6 rpm. The densities (g/cm³) of certain oligomers were measured with a BYK-Gardner pycnometer. The percentage of NVW of the synthesized oligomers was determined upon heating a sample placed in aluminum dish at 110°C for 1 h, in an air-circulated oven (ASTM D2369-95). The hydroxyl values of the oligomers were determined according to the ASTM D-1957 method.

2.2. Materials

DI (99%), HD (97%), MP (99%), NG (99%), DD (99%), zinc acetate dihydrate (99 + %) and dibutyltin dilaureate (95%), were purchased from the Aldrich Chemical Company and used as supplied.

2.3. Synthesis of oligoesters — general experimental procedure

Dimethyl isophthalate, diol(s) and a catalytic amount of zinc acetate dihydrate were placed in a round-bottomed flask equipped with a Dean–Stark trap, mechanical stirrer, thermometer, N₂ inlet and a condenser. The mixture was heated under a stream of N₂, in temperatures from 140 up to 210°C for 5 h from the moment MeOH began to collect. The molten product was quickly poured into a steel container to cool and then kept in a vial at room temperature. The various products were obtained either as white solids or transparent resins or transparent liquids (see the synthesis of hydroxyl-terminated isophthalate-based oligoesters in Scheme 1).

2.4. Synthesis of the reference oligoester (RefOL)

Dimethyl isophthalate (582.57 g, 3.00 mol), 1,6-hexanediol (508.17 g, 4.30 mol) and zinc acetate dihydrate (2.18 g, 0.20% w/w of total reactant weight) were charged into a reactor equipped with a Dean–Stark trap, mechanical stirrer, thermometer, N₂ inlet and a condenser. The mixture was flushed with N₂, heated to 140 and then gradually to 200°C during 5 h, while collecting methanol in the Dean–Stark traps. When visible methanol collection ended, the temperature was increased to 210°C for 30 min. The warm product was poured into a metallic container before it solidified to a white partly crystalline low-melting solid (942.91 g, yield = 98.9%, NVW = 98%).

$$M_n = 1385, \quad M_w = 2439, \quad M_p = 2420, \quad M_z = 3654,$$

$M_{z+1} = 4878$, $M_v = 2273$, $D = 1.76$. Excess of HD = 1.60% w/w. HO-value = 164 mg KOH equivalent to a 1-g sample. $T_g = -37^\circ\text{C}$, $T_m = 39^\circ\text{C}$ (onset temperatures determined by MDSC). FT-IR (cm⁻¹): 3378 (O–H stretching); 1734 (C=O); 1610 (benzene ring); 1405 (O–H deformation); 1076 (C–O–C stretching).

¹H NMR (CDCl₃) δ : 8.67 (s, aromatic proton in between the –C=O); 8.22 (m, aromatic protons in *ortho*-position to each of –C=O); 7.52 (m, aromatic proton in *meta*-position to each of –C=O); 4.36 (m, –CH₂– protons of the HD segment at the carbon atom in *a*-position to –O–C=O); 3.65 (m, –CH₂– protons of the HD segment at the carbon atom in *a*-position to –OH); 2.12 (b, hydroxyl protons of the HD segment); 1.80–1.47 (m, –the rest CH₂– protons of the HD segment).

¹³C NMR (CDCl₃) δ : 165.64 (carbons of –C=O); 133.69 (aromatic carbon in between the –C=O); 130.81 (aromatic carbons in *ortho*-position to each of –C=O); 128.59 (aromatic carbon in *meta*-position to each of –C=O); 65.28 (–CH₂– carbon attached to the –OH of the HD segments); 62.30 (–CH₂– carbon of the HD segment in *a*-position to the –O–C=O); 32.57 (–CH₂– carbon in β -position to –OH of the HD segment); 28.61 (–CH₂– carbon of the HD segment in β -position to –O–C=O); 25.84 (–CH₂– carbon of the HD segment in *c*-position to –OH); 25.74 (–CH₂– carbon of the HD segment in *c*-position to –O–C=O).

2.5. Synthesis of the oligoester L-311

Dimethyl isophthalate (582.57 g, 3.00 mol), 1,6-hexanediol (531.81 g, 4.50 mol), 2-methyl-1,3-propanediol (405.54 g, 4.50 mol) and a catalytic amount of dibutyltin dilaureate (1.52 g, 0.10% w/w of total reactant weight) were placed in a round-bottomed flask equipped with a Dean–Stark trap, mechanical stirrer, thermometer, N₂ inlet and a condenser. The mixture was heated under a stream of N₂ at 200–210°C for 5 h, from the moment methanol began to collect. The transparent liquid product was quickly poured into a steel container to cool and then kept in a vial at room temperature (1305 g, yield = 98.3%, NVW = 82%, $n_{25^\circ\text{C}} = 2010$ cP, $d_{25^\circ\text{C}} = 1.0984$ g/cm³, VOC = 1.66 lbs/gal).

$M_n = 538$, $M_w = 719$, $M_p = 388$, $M_z = 1016$, $M_{z+1} = 1343$, $M_v = 710$, $D = 1.33$. Excess of diols = 1.98% w/w (HD 1.49% w/w, MP 0.49% w/w). HO-value = 355 mg KOH equivalent to a 1-g sample. $T_g = -72^\circ\text{C}$ (onset temperature determined by MDSC). FT-IR (cm⁻¹): 3348 (O–H stretching); 1724 (C=O); 1613 (benzene ring); 1390 (O–H deformation); 1040 (C–O–C stretching).

¹H NMR (CDCl₃) δ : 8.65 (s, aromatic proton in between the –C=O); 8.23 (m, aromatic protons in *ortho*-position to each of –C=O); 7.54 (m, aromatic proton in *meta*-position to each of –C=O); 4.38–4.35 (m, –CH₂–protons of the MP and HD segment at the carbon atom in *a*-position to –O–C=O); 4.15 (b, hydroxyl proton of the MP segment); 3.77–3.60 (m, –CH₂– protons of the MP and HD segment at the

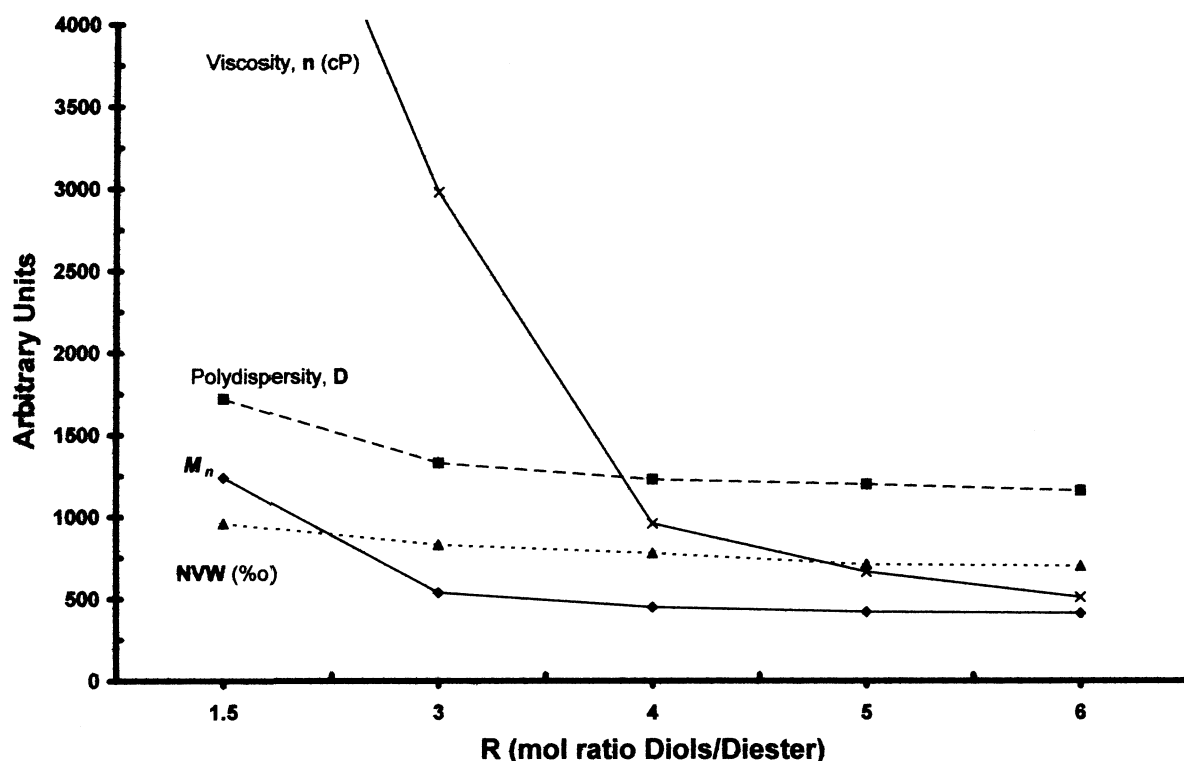


Fig. 1. The change in n (cP), D ($\times 10^3$), M_n and NVW (%) of a series of oligoesters ($R_d = \text{mol MP/mol HD} = 1/3$) vs. R (mol diols/diester).

carbon atom in *a*-position to $-\text{OH}$); 2.16 (b, hydroxyl protons of the HD segment); 1.82 (m, $-\text{CH}-$ proton of the MP segment); 1.55–1.38 (m, $-(\text{CH}_2)_4-$ protons of the HD segment); 1.08–0.89 (m, $-\text{CH}_3$ protons of the MP segment).

^{13}C NMR (CDCl_3) δ : 166.06 (carbons of $-\text{C}=\text{O}$); 133.73 (aromatic carbon in between the $\text{C}=\text{O}$); 130.76 (aromatic carbons in *ortho*-position to each of $-\text{C}=\text{O}$); 128.66 (aromatic carbon in *meta*-position to each of $-\text{C}=\text{O}$); 66.53 ($-\text{CH}_2-$ carbon of the MP segment attached to the $-\text{OH}$); 65.45 ($-\text{CH}_2-$ carbon of the MP segment attached to the $-\text{O}-\text{C}=\text{O}$); 64.08 ($-\text{CH}_2-$ carbon of the HD segment attached to the $-\text{OH}$); 62.30 ($-\text{CH}_2-$ carbon of the HD segment attached to the $-\text{O}-\text{C}=\text{O}$); 37.27 ($-\text{CH}-$ carbon of the MP segment); 35.55 ($-\text{CH}_2-$ carbon of the HD segment in β -position to $-\text{OH}$); 32.48 ($-\text{CH}_2-$ carbon of the HD segments in β -position to $-\text{O}-\text{C}=\text{O}$); 28.60 ($-\text{CH}_2-$ carbon of the HD segment in *c*-position to $-\text{OH}$); 25.72 ($-\text{CH}_2-$ carbon of the HD segment in *c*-position to $-\text{O}-\text{C}=\text{O}$); 13.27 ($-\text{CH}_3$ carbon of the MP segment).

3. Results and discussion

3.1. Studies of the effect of the transesterification reaction parameters on the properties of the hydroxyl-terminated isophthalate-based oligoesters

A series of oligoesters was synthesized in a straight-

forward process via the transesterification reaction (Scheme 1). Dimethyl isophthalate (DI) reacted under various molar ratios with different diols such as 1,6-hexanediol (HD), 2-methyl-1,3-propanediol (MP), neopentyl glycol (NG) and 1,10-decanediol (DD) either separately with one of the diols or with a mixture of the aforementioned diols. The diols were always in excess and if we denote the ratio of the moles of the diol(s) to the moles of the diester by R , then in the reactions we studied, R was equal to 2, 3, 4, 5 and 6. Different molar ratios of diols (R_d) were used in the cases where a mixture of diols was reacted with DI.

More specifically, the effect of different reaction parameters such as:

- the molar ratio diol(s)/diester (R);
- the molar ratio of diols (R_d) (when a mixture of diols was used);
- the species of the diol;
- the reaction time;
- the heating procedure;
- the specie and amount of catalyst;

on the physical state (solid or liquid), the polydispersity (D), the M_n , the viscosity (n , cP) and the NVW (% weight) of the synthesized oligoester has been studied.

The effect of every specific reaction parameter on the properties of the oligoesters was studied separately, while all the other parameters remained constant. The heating procedure that has been applied in all cases except in those where it was studied as a reaction parameter, was

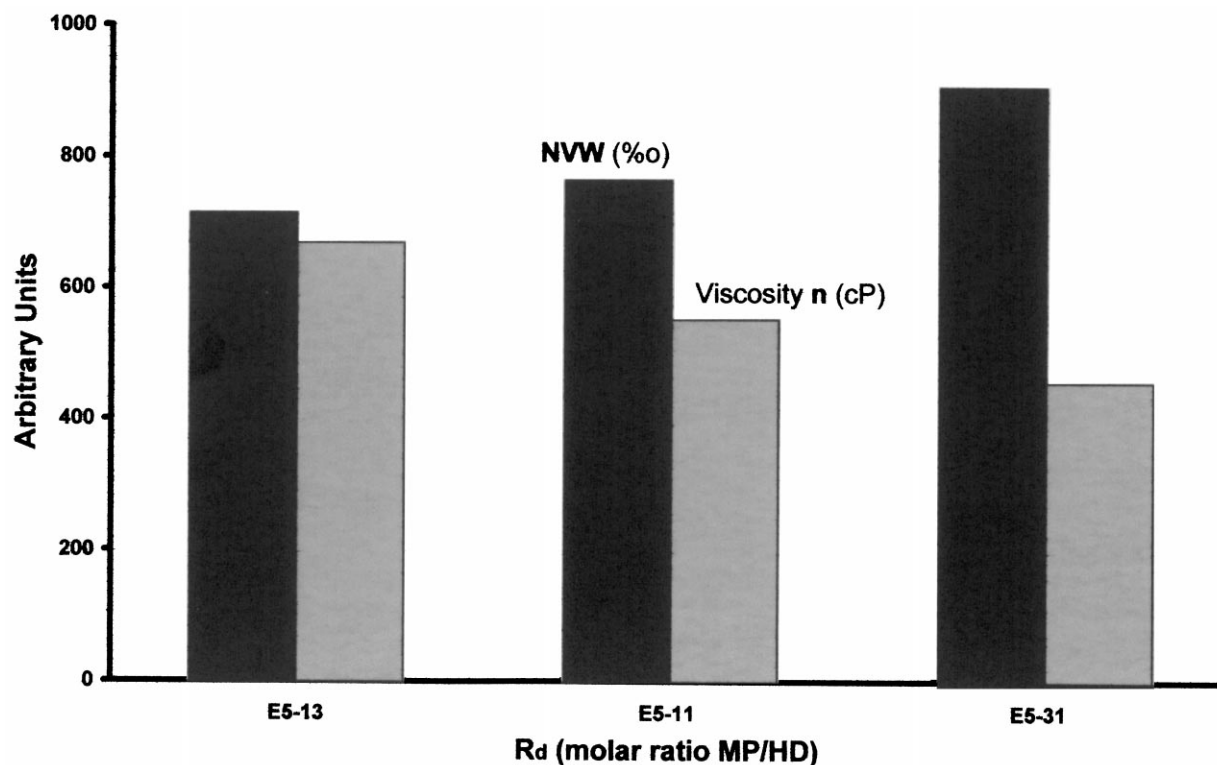


Fig. 2. The change in n (cP) and NVW (%) of three oligoesters with $R = 5$ and different R_d (= mol MP/mol HD) = 1/3, 1/1 and 3/1.

the one described in Section 2.3. The changes that each of the reaction parameters caused in the polydispersity (D), the M_n , the viscosity (n) and the NVW of the produced oligoester are presented in Figs. 1–8.

More specifically, Fig. 1 presents the effect of the excess of diols on D , M_n , n and NVW. It is more than obvious that by increasing R when R_d = (mol MP/mol HD) = 1/3, n and M_n decreased dramatically for $R > 1.5$. Polydispersity (D) and

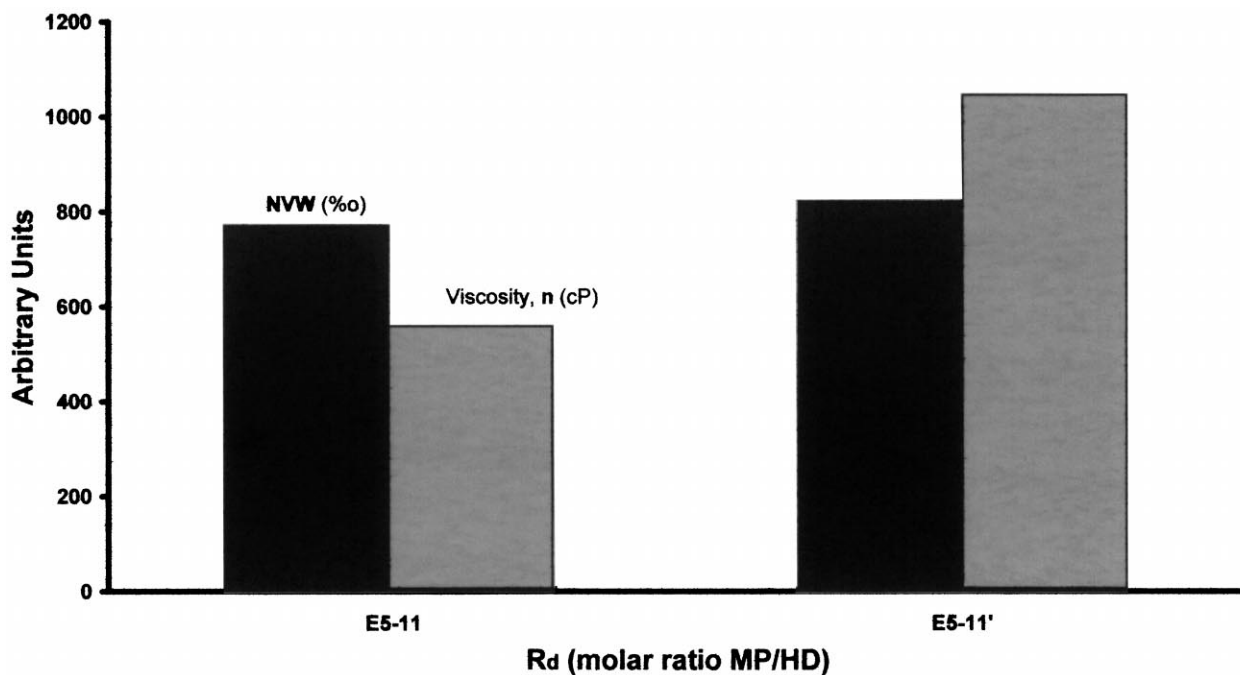


Fig. 3. The change in n (cP) and NVW (%) of the oligoesters E5-11' ($R = 5$ and R_d (mol NG/mol HD) = 1/1), and E5-11 ($R = 5$ and R_d (mol MP/mol HD) = 1/1).

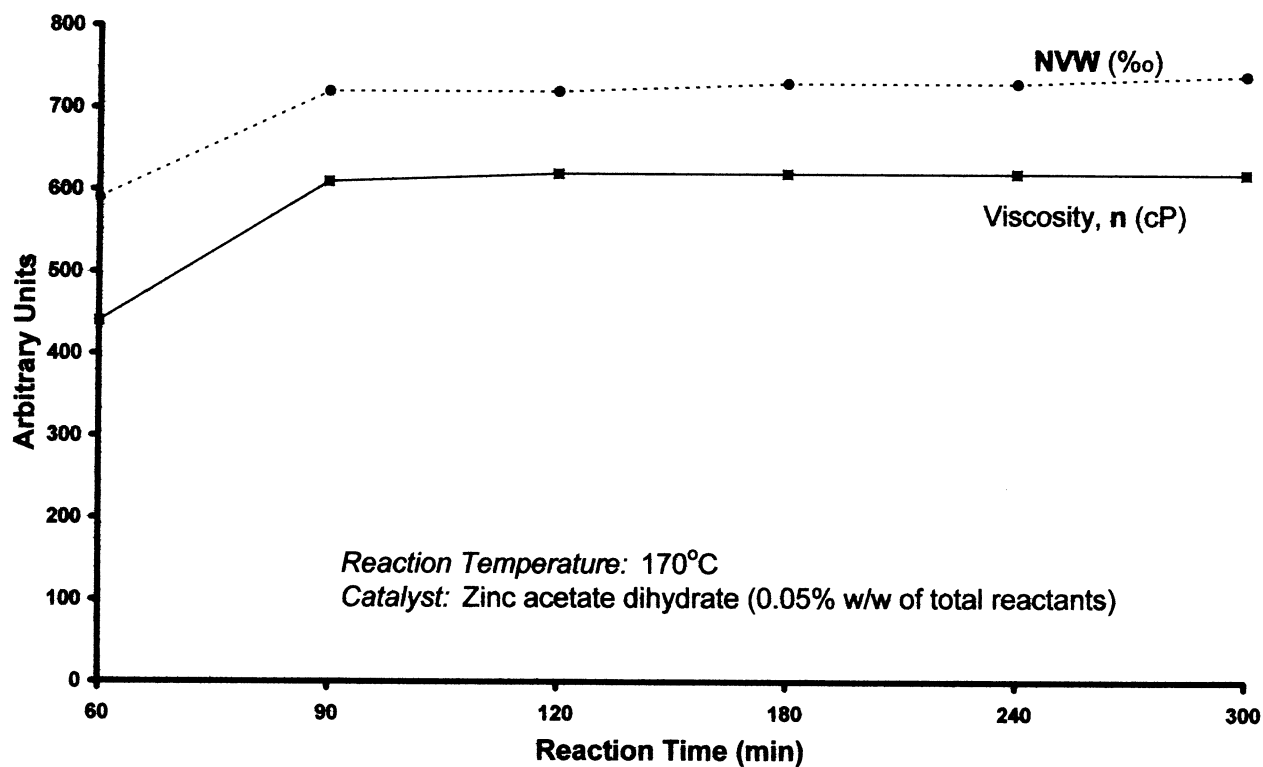


Fig. 4. The change in n (cP) and NVW (‰) of an oligoester ($R = 5$ and $R_d = \text{mol MP/mol HD} = 1/3$) vs. the reaction time at 170°C, when zinc acetate dihydrate (0.05% w/w of total reactants) was used as catalyst.

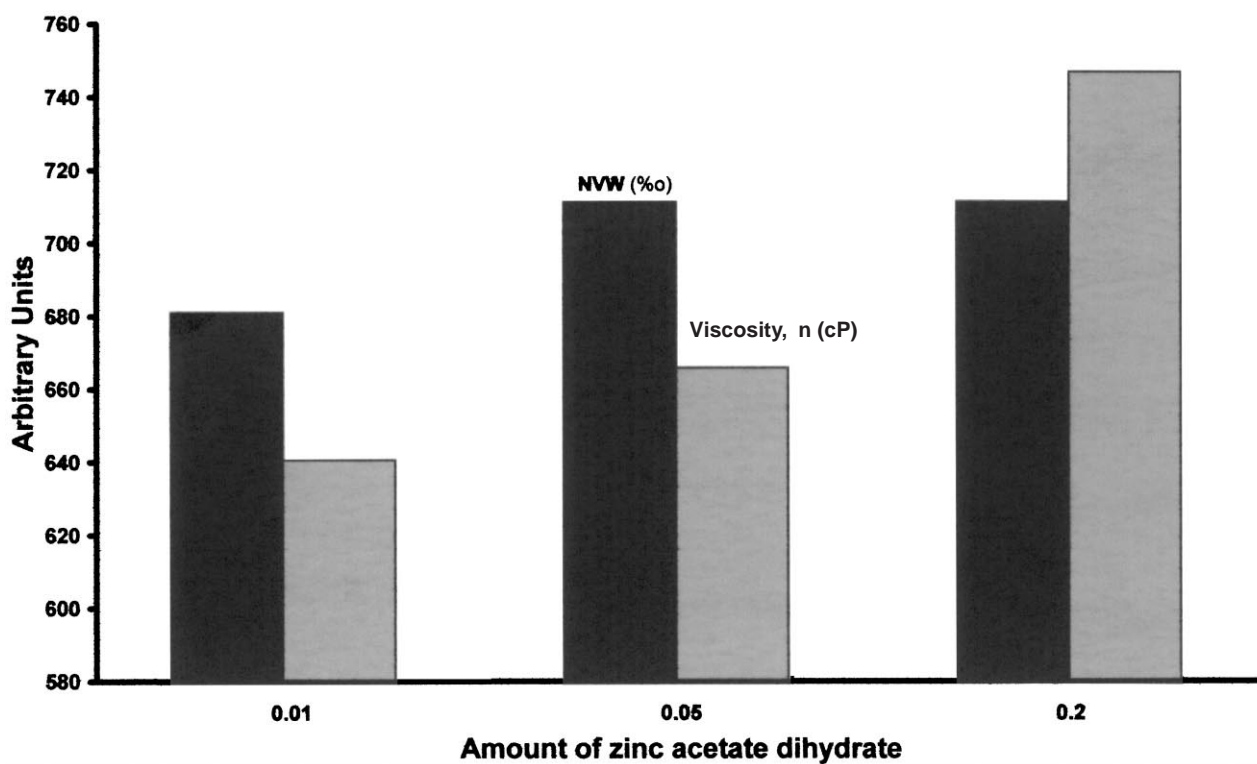


Fig. 5. The change in n (cP) and NVW (‰) of an oligoester ($R = 5$ and $R_d = \text{mol MP/mol HD} = 1/3$) vs. the amount of zinc acetate dihydrate used as catalyst.

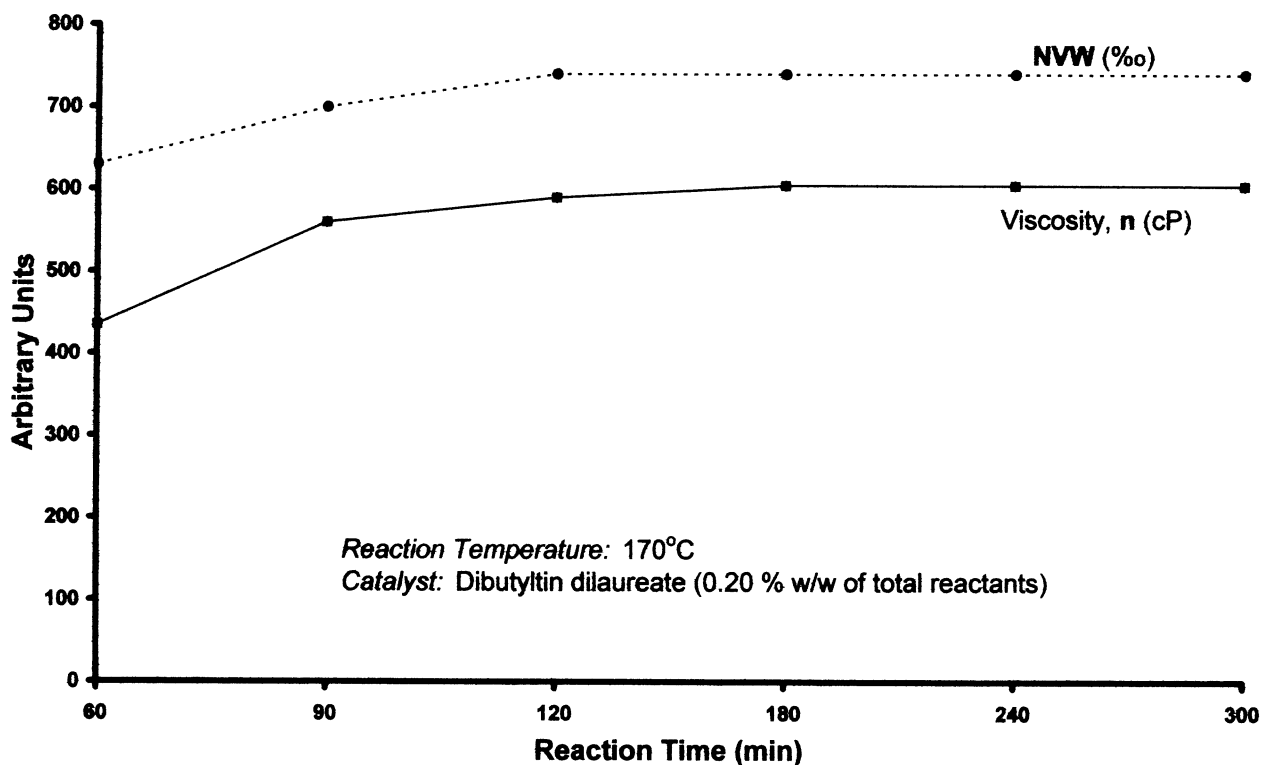


Fig. 6. The change in n (cP) and NVW (%) of an oligoester ($R = 5$ and $R_d = \text{mol MP/mol HD} = 1/3$) vs. the reaction time at 170°C , when dibutyltin dilaureate (0.20% w/w of total reactants) was used as catalyst.

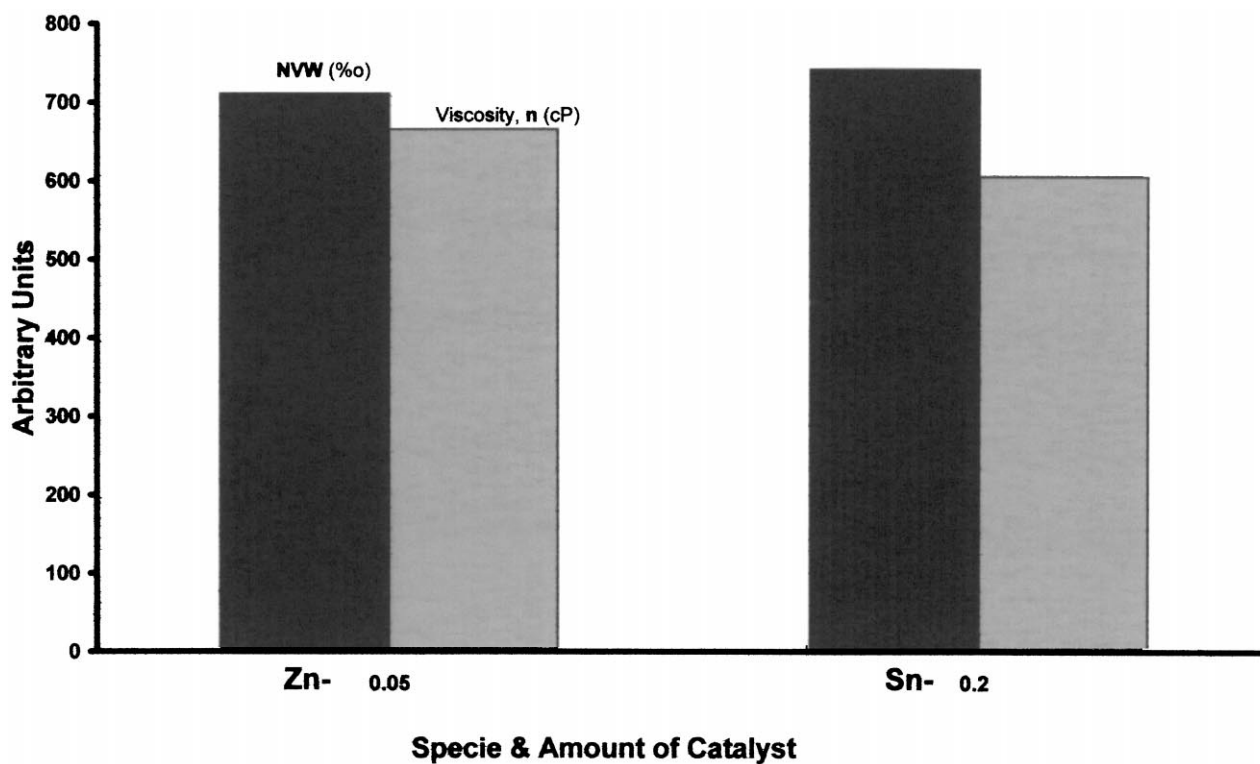


Fig. 7. The change in n (cP) and NVW (%) of an oligoester ($R = 5$ and $R_d = \text{mol MP/mol HD} = 1/3$), which was synthesized using different catalysts (Zn 0.05% w/w (Zn-0.05) and Sn 0.20% w/w (Sn-0.2)) (the quantities of the catalysts are referred to the total reactants).

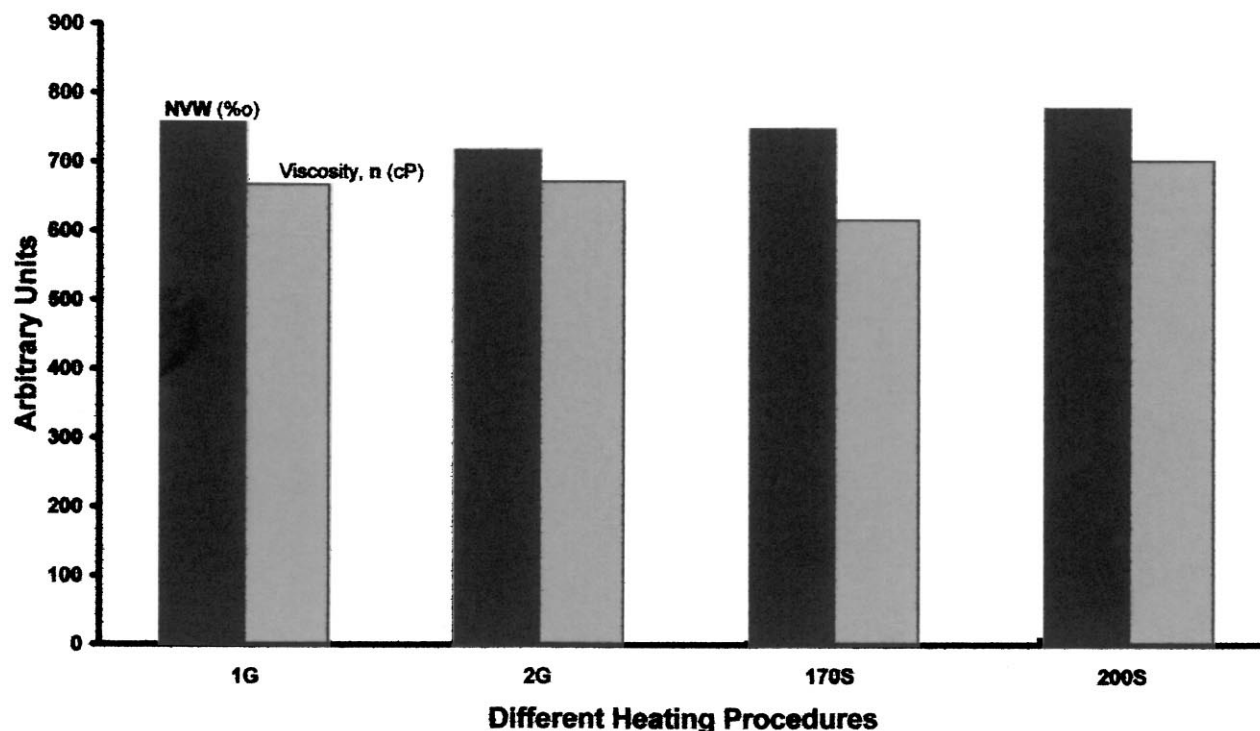


Fig. 8. The change in n (cP) and NVW (%) vs. different heating procedures (1G, synthesis of RefOL; 2G, synthesis of oligoesters (general procedure); 170S, heating at 170°C for 4 h; and 200S, heating at 200°C for 4 h).

NVW followed the same pattern but the changes were not so dramatic. Of all the reaction parameters studied independently of the diols used in the reaction, this is the parameter that most affected the M_n and D . It has to be stressed that for $R < 2$, the synthesized oligoesters were obtained either as crystalline white solids or as extremely viscous transparent resins. Obviously, the synthesis of liquid HO-terminated isophthalate-based oligoesters could be accomplished only when a big excess of diol(s) was used.

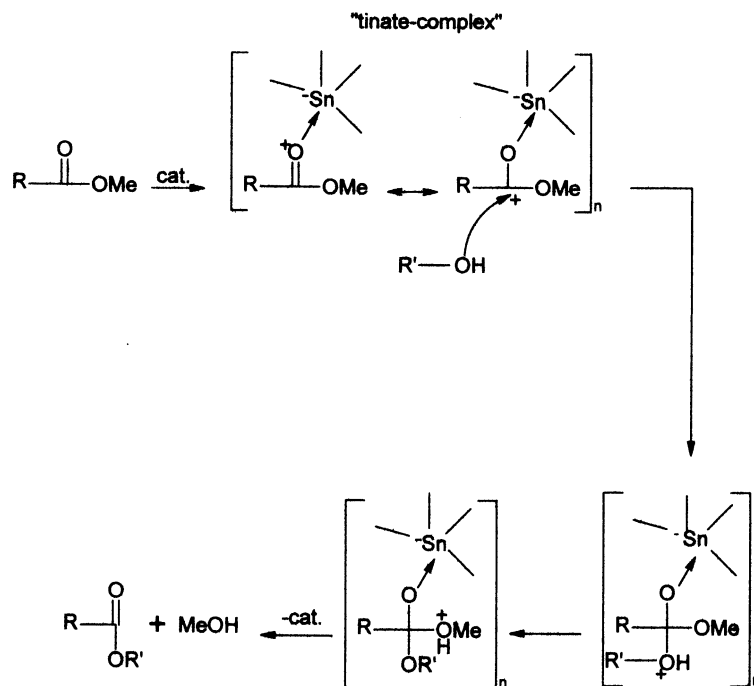
In cases in which $R = 5$, by decreasing the moles of HD in a mixture with MP ($R_d = \text{mol MP/mol HD} = 1/3, 1/1$ and $3/1$), no significant changes were observed on the D and M_n of the synthesized liquid oligoesters, while the n decreased and the NVW increased (Fig. 2). When $R = 3$, the change in n followed the same pattern but NVW remained almost constant. It became obvious that the introduction of MP in the reaction mixture was necessary in order to obtain liquid oligoesters. In all reactions where only DI reacted with only HD, even when HD was in high excess ($R = 4$), the oligoester was obtained as a partly crystalline white solid.

When MP was substituted by NG in a reaction mixture with HD and DI ($R = 3$ and $R_d = 1/3$), the synthesized liquid oligoester (E5-11') presented an increased viscosity and a higher NVW value than the liquid oligoester (E5-11) obtained from MP (Fig. 3). No significant changes were observed in D and M_n . Solid oligoesters were obtained when DD was used instead of MP, in reactions where $R = 5$ and $R_d = 4/1$.

When a transesterification ($R = 3$ and $R_d = 1/3$ MP/HD)

took place on steady heating at 170°C for 5 h, the viscosity and NVW of the synthesized liquid oligoester increased during the first 90 min (Fig. 4). From that point on, both remained almost constant. When the reaction temperature was 200°C for 5 h, the change in viscosity and NVW followed almost the same pattern, but the values of viscosity and NVW were higher than those of the previous reaction. In both reactions zinc acetate dihydrate (0.05% w/w of total reactant weight) was used as catalyst. The phenomenon is not surprising because the viscosity of the bulk changes rapidly during the reaction. In other words, the viscosity depends upon the degree of conversion and the rate of the reaction. Both were dramatically changed within the first 90 min. This is an indication that: (a) products with less conversion present considerably lower viscosities; and (b) we could obtain products of a certain degree of conversion and viscosity value by determining the reaction time (products derived from the reaction of the same reaction mixture with lower degrees of conversion presented almost half the viscosity values of corresponding products with higher degrees of conversion). No significant changes were observed in D and M_n .

The effect that the species and amount of Lewis acid catalyst used in the transesterifications had on the properties of the oligoesters were investigated also. The mechanism of the acid-catalyzed transesterification is described as an acyl-cleavage acid-catalyzed bimolecular (Aac2) and is presented in Scheme 2 (where dibutyltin dilaurate is used as catalyst). It became evident that by increasing the amount



Scheme 2.

of the catalyst (either zinc acetate dihydrate or dibutyltin dilaureate), the viscosity increased significantly while the NVW remained almost constant (Fig. 5).

When the reaction took place on steady heating at 170°C and dibutyltin dilaureate (0.20% w/w of total reactants) was used as catalyst, n and NVW followed the pattern presented in Fig. 6. More specifically, both increased during the first 180 min, while the same measures, when zinc acetate dihydrate was used as catalyst, increased for only the first 90 min (Fig. 5).

Upon comparing the data of Figs. 5 and 6, it becomes evident that although the quantity of the tin catalyst was four times more than that of the zinc catalyst, the change of the viscosity, which is a measurement of the progress and the rate of the reaction, was still faster in the case where zinc acetate dihydrate was used as catalyst. Zinc acetate dihydrate proved to be a “stronger” catalyst than dibutyltin dilaureate.

Moreover, it was shown that the milder the Lewis acid catalyst, the lower the viscosity and the NVW of the liquid oligoesters (Fig. 7).

Steady heating (S) at high temperatures (170 and 200°C) using the same amount of catalyst afforded liquid oligoesters with slightly higher viscosities and higher NVW than those obtained upon gradient heating (G) (see Section 2.3 or Section 2.4) (Fig. 8). This parameter always has to be evaluated with respect to the species and the amount of catalyst used in the reaction.

3.2. Reaction parameters and NVW values

It has been observed also that the NVW values of the

oligoesters decreased as: (a) R increased, and (b) the quantity of HD in the system decreased. This behavior could be attributed to the fact that high R values lead to higher excesses of free diols, which were actually the volatile components of the product. Upon comparing the boiling points of the two diols ($\text{bp}_{\text{HD}} (250^\circ\text{C}) > \text{bp}_{\text{MP}} (213^\circ\text{C})$), it became evident why the NVW values of the products were affected by the quantity of HD in the reaction mixture, as the latter is relatively less volatile than MP.

3.3. Reaction parameters and product viscosity

The viscosity of the various synthesized oligoesters was affected by: (a) the R values, (b) the species and the amount of the Lewis acid catalyst used in the transesterification, (c) the quantity of HD in the reaction mixture and the chemical structure of the diols (experiment with NG — a relatively more “branched” structure — when it substituted MP in a reaction mixture), and (d) the heating procedure and reaction time. The high R values resulted in products with significantly lower M_n and M_w and, of course, this led to products with lower viscosities. As for the influence that the selection of a certain Lewis acid catalyst could have on the viscosity of the product, it is well known that changing the Lewis acid may have dramatic effects on the rate of the reaction and the product distribution [9].

It has been noticed that lower viscosity values were obtained by increasing the quantity of HD in the system. On the other hand, when a more “branched” diol (NG) was used instead of MP in the reaction mixture, then the viscosity increased significantly. This behavior could be

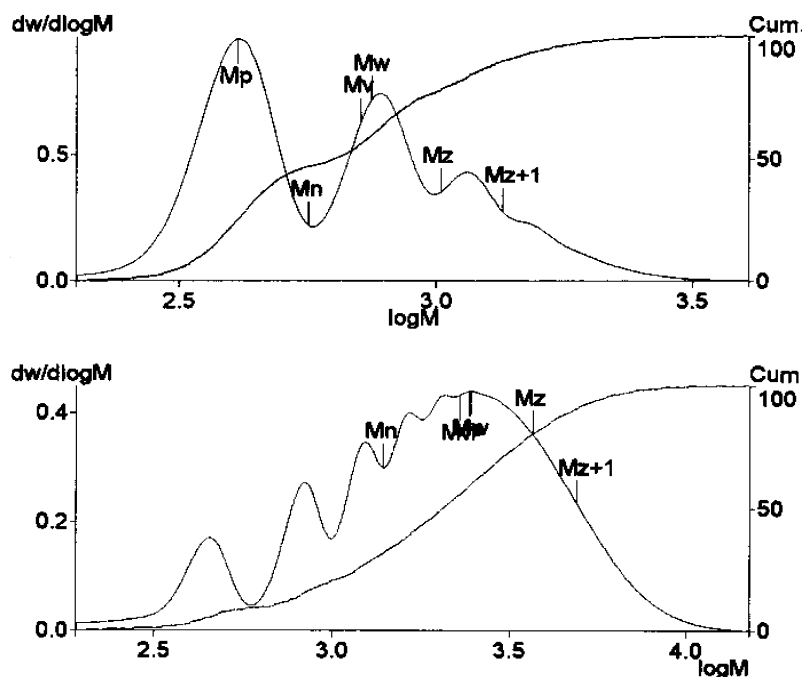


Fig. 9. Gel permeation chromatographs ($dw/d\log M$ vs. $\log M$) of L-311 (top) and RefOL (bottom).

attributed to the fact that HD (linear diol) favors the formation of liquid crystals. It is well known that liquid crystals present lower viscosity than do their isotropic liquids. In addition, the low M_n and M_w of the newly synthesized liquid oligoesters could contribute to this and favor further the formation of some mesogenic units. If formed, those LC oligomers would belong to the category of main-chain LCP with mesogens separated by flexible spacers. In addition, the DSC thermogram of L-311 on cooling presented an exothermic peak ($\Delta H = 4.64$ J/g), which probably could be attributed to crystallization. Of course, this is just an indication of the existence of some degree of liquid crystallinity in our low-molecular HO-terminated liquid oligoesters and further investigation is needed mainly using hot-plate polarizing microscopy and wide-angle X-ray diffractometry.

As regards the influence that the “branching” of the diols may have on the viscosity (in case in which we have some degree of liquid crystallinity), this is generally complicated by both steric and polar effects. In our case, only the first could have an effect on liquid crystallines. The steric effect generally results in reducing the thermal stability of the mesophase and involves the following molecular contributions: (a) a broadening of the mesophase group by the substituent and, therefore, a decrease in the overall length-to-width ratio; (b) a decrease in the coplanarity of adjacent units in the mesogenic group because of steric interactions between substituents; and (c) a tendency for the substituents to force apart mesogenic units in neighboring polymer chains because of their space requirements.

The effect of the reaction temperature on the viscosity of the final product probably has to do also with the aforemen-

tioned phenomenon. These liquid crystals (if formed) belong to the category of thermotropic liquid crystals, the formation of which is influenced by the temperature of the melt. The higher the temperature of the melt, the more favorable the transition to the corresponding isotropic liquid that presents higher viscosity than its liquid crystals becomes. Therefore, the observed viscosity of a liquid oligoester may increase at higher reaction temperatures.

3.4. Studies on the properties of RefOL and L-311

To obtain a better insight of the changes observed in the properties and characteristic measures, which can be seen between RefOL and L-311, we investigated the relative reactivity of HD and MP in reaction with DI. The excess (% w/w) of the diols was determined for three oligoesters (OL-1, OL-2, and OL-3) with gas chromatography. The heating procedure and the reaction time were the same in all these reactions (steady heating at 200°C, for 4 h).

In the case of the liquid OL-1 where $R = 3$ and R_d^{in} (initial molar ratio) = mol HD/mol MP = 1/1, it was found that the final molar ratio (R_d^{fin}) of the excess of the diols in the synthesized corresponding oligoester was 2.32/1. Subsequently, if F denotes the proportion ($R_d^{\text{fin}}/R_d^{\text{in}}$), then F_1 in the case of OL-1 was equal to 2.32. The solid OL-2 has been prepared when $R = 3$ and $R_d^{\text{in}} = 3/1$ and the corresponding values of R_d^{fin} and F_2 were 7.88/1 and 2.63, respectively. Here, it has to be stressed that in the reaction for the synthesis of OL-1, dibutyltin dilaureate was used as catalyst while in that of OL-2, the catalyst was zinc acetate dihydrate. When $R = 5$ and $R_d^{\text{in}} = 1/3$ (liquid oligoester OL-3), R_d^{fin} and F_3 were 1/1.14 and 2.63, respectively. From all these

GC experimental data we may conclude the following (relations (1)–(3)):

$$F_1 < F_2 = F_3 \quad (1)$$

The reaction rate of MP (U_{MP}) was greater than that of HD (U_{HD}) and when zinc acetate dihydrate was used as catalyst, the reaction rate of MP (U_{MP}^{Zn}) was greater than that of MP (U_{MP}^{Sn}) when dibutyltin dilaureate catalyzed the reaction:

$$U_{MP} > U_{HD} \quad (2)$$

$$U_{MP}^{Zn} > U_{MP}^{Sn}, \quad (F_2 > F_1) \quad (3)$$

Experimental GC data, where the variable of the reaction conditions was the heating procedure, verified that different heating procedures had no effect on the relative reactivity of the diols. These results can lead to the following assumptions: (a) the reactivity of MP is greater than that of HD under any experimental condition; (b) the catalyst that is used in the reaction could affect the relative reaction rates of the diols to some extent — the “stronger” the Lewis acid (catalyst), the higher the reaction rate of the more reactive diol; and (c) the percentage of the excess of diols in the synthesized oligoester does not depend only on R but also on R_d , as well. Actually, it is the R_d^{in} value that is most crucial in determining the percentage of the excess of free diols in the product. At a certain R and R_d^{in} for oligoesters derived from the reaction of DI with a mixture of HD and MP, we may also predict (with respect to the catalyst we use), the R_d^{fin} and/or the molar and weight ratio of the free diols of another R_d^{in} by applying the following equations:

$$R_d^{fin} = 2.63R_d^{in}$$

or

$$t(\text{mol HD/mol MP}) = 2.63R_d^{in}$$

(in oligoesters of a certain R and when zinc acetate dihydrate is used as catalyst). Equations based on the same idea and experimental methodology can be extrapolated even when other starting materials are used for the synthesis of hydroxyl-terminated oligoesters.

The polydispersity of L-311 ($D = 1.33$) was lower than that of RefOL ($D = 1.76$). This could be explained from the fact that the M_n of L-311 was three times lower than that of its solid counterpart (RefOL). In the gel permeation chromatograph of L-311 (Fig. 9), three very well-separated peaks of different heights were recorded. These three peaks corresponded to M_n values of 388 (first peak), 719 (second peak) and 1100 (third peak), respectively (the numbering of the peaks proceeds from left to right).

The higher excess of diols, the introduction of MP in the reaction mixture and the significant difference between the reaction rates of the two diols are obviously the reasons for the difference between both the above GP chromatographs. In the GP chromatograph of RefOL (Fig. 9), the molecular weights are shifted to higher values because of the aforementioned reasons. The introduction of the more reactive

MP molecules in the reaction mixture leads to a much faster reaction with the DI molecules, which subsequently results in the “blocking” of a significant number of DI molecules with the synthesis of HO-terminated trimers of the composition: MP–DI–MP. Since these trimers are formed, they become relatively less “flexible” for further reaction with other molecules of DI. In other words, trimers (first peak) of the aforementioned composition are formed very fast, “blocking” a large number of DI molecules and “preventing” them from reacting with the HD molecules during the first stages of the transesterification. Then, some of these trimers begin to react with other DI molecules to form heptamers or, subsequently, nonamers (third peak) of compositions where the presence of HD (the less reactive diol) is more intense. The second peak corresponds to pentamers, which are mainly derived upon reaction of trimers of the sequence: (a) MP–DI–HD, (b) HD–DI–HD, or (c) MP–DI–MP with one DI molecule and subsequently of another — mainly HD — diol molecule. The composition of these pentamers is probably closer to the following: (trimer a or b or c)–DI–HD. The same pattern of the three very well-distinguished peaks was also recorded in the GP chromatograph of an oligoester synthesized from a mixture of DI, HD and NG. In the case of an oligoester, which was prepared from the reaction of DI and HD with the same molar ratio as that of L-311 ($R = 3$), the GP chromatograph presented the same pattern as that of RefOL.

Related to the different reaction rates and the huge difference in the melting points of the two diols ($mp_{MP} = -91$ and $mp_{HD} = 48^\circ\text{C}$) used for the preparation of L-311, was the observed difference in the physical state of RefOL (solid) and that of L-311 (liquid). As we showed previously, HD reacts much slower than MP. Subsequently, the more the initial quantity of HD in the initial composition of the reaction mixture, the more the quantity of unreacted HD in the final product (e.g. in the case of OL-2 where $R = 3$ and $R_d^{in} = \text{mol HD/mol MP} = 3/1$, the excess of HD was 10.23% w/w and that of MP 0.98% w/w). These facts could lead to the assumption that the “richer” the reaction mixture in HD, the more favored the crystallization of the synthesized oligoester. This is due to the fact that the remaining unreacted HD begins to crystallize slowly prior to any possible crystallization of the oligomer itself ($mp_{HD} = 48 > mp_{RefOL} = 39^\circ\text{C}$), providing the system with the necessary crystallites for a subsequent extended crystallization of the product. MP does not contribute to the crystallization of the oligoester, as its melting point is -91°C . It is not accidental that even reactions with low R values ($1 < R < 2$) and where the maximum quantity of HD in the system did not exceed the equimolar ratio of MP, resulted in highly viscous, transparent resins and not in white solids. No further crystallization was observed in these products when they were kept at room temperature. In certain transesterifications, even when a big excess of HD was used but with no MP, the synthesized oligoester crystallized. The unreacted HD (1.60% w/w) of the RefOL was responsible

for its very quick crystallization. It becomes evident why it is not possible to synthesize liquid isophthalate-based oligoesters using only DI and HD under any R value. On the other hand, however, it is obvious that a liquid oligoester can be prepared easily when one or more of the diols (e.g. MP) have a melting point lower than the room temperature and are used in an appropriate equimolar ratio in a mixture with diols, which present higher melting points.

The newly synthesized liquid oligoester L-311 presented — not surprisingly — a significantly lower glass transition temperature than RefOL of about 35°C. The difference in T_g s could be attributed to the big difference in M_n s. RefOL had M_n almost three times higher than that of L-311 and the dependence of T_g upon M_n is well known. The following equation describes this relation exactly [10]:

$$T_g = T_g^{00} - KM_n^{-1}$$

where K denotes a constant and T_g^{00} corresponds to the glass transition temperature of a polymer with theoretically infinite M_n .

The synthetic method that we applied for the synthesis of L-311 was the one we considered as the most adequate for combining all the experimental data that could guarantee the production in high yield and high conversion, of a high-solids liquid HO-terminated isophthalate-based oligoester with the lowest possible viscosity and the highest NVW values. The preparation and investigation of the physical and chemical properties of high-solids mar-resistant clear-coats or pigmented coatings using the newly synthesized L-311 as a binder will be among our aims for the near future.

4. Conclusions

- (a) The molecular distributions of the newly synthesized liquid oligoesters are narrower than that of the reference solid oligoester.
- (b) The molecular weight distribution of the product is mainly affected by R and to some extent by the species and the molar ratio (R_d) of the diols, as well. The higher the value of R , the lower the value of NVW, M_n and the viscosity of the liquid oligomer.
- (c) The higher the molar ratio of HD in the system, the lower the viscosity of the liquid oligomer. The NVW follows the same pattern for R values higher than 4.
- (d) Even with high R values and in big excesses of HD, a system without MP crystallizes slowly, even when kept at room temperature.

(e) The more bulky the side groups a diol possesses, the higher is the viscosity of the synthesized liquid oligoester.

(f) The selection of the species and the amount of Lewis acid catalyst are of great importance as regards the physical properties of the products and always has to be considered along with the heating procedure and the reaction time.

(g) The NVW values depend not only on R and R_d , but also on the relative boiling points of the diols presented in the system.

(h) The reactivity of MP is higher than that of HD and this could be also an indication that β -substituted diols react more readily with diesters than do unsubstituted diols.

(i) If the aim is to obtain a high-solids liquid isophthalate-based oligoester with high conversion, the lowest possible viscosity and the highest NVW in high yields, then R has to be equal to/greater than 3 and R_d (mol HD/mol MP) does not have to exceed the value 1. The reaction temperature cannot exceed 210°C because higher reaction temperatures may result in thermal decomposition of the synthesized oligoester.

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