Synthesis and Characterization of Imide End-Capped Oligoesters of Terephthalic Acid and 2-Methyl-2-Propyl-1,3-Propanediol

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Synopsis

Hydroxytelequelic oligoesters of molecular weight (M_n) between 500 and 3000 were prepared from dimethylterephthalate (DMT) and 2-methyl-2-propyl-1,3-propanediol (MPPD) by ester interchange polycondensation. They were modified by reaction of their end hydroxyl groups with *N*-(4-chlorocarbonylphenyl)maleimide and *N*-(4-chlorocarbonylphenyl)nadimide. Spectroscopic (NMR), chromatographic (GPC), and calorimetric (DSC) analyses demonstrated that MPPD oligoterephthalates are less reactive than previously used glycols (diethylene glycol, DEG) and only nadimide-modified oligomers could be readily synthesized. Attempts to introduce maleimide groups at the chain ends led to crosslinked materials. Furthermore, some relationships between molecular weight and properties (T_g, thermal stability, etc.) could be outlined. The oligomers, unmodified and modified, proved to be essentially amorphous.

INTRODUCTION

In a previous study we reported on the functionalization of poly(diethyleneglycol terephthalate) (PDET) oligomers by means of nadimide and maleimide end-capping groups.[1]

PDET is a polymer that shows some particular characteristics such as solubility in organic solvents, inability to crystallize from the melt, and possibility of modification through its hydroxyl end groups. These properties have shown that it is very adequate to use PDET as a model for conformational studies and for the preparation of polymer model networks.[2]

A polyester that may show similar properties is the polyterephthalate of a branched glycol: 2-methyl-2-propyl-1,3-propanediol (MPPD). This diol has been successfully used in the preparation of polyesters[3] and copolyesters.[4-6] It offers, against other possible candidates (e.g., 1,2-propyleneglycol), the advantage of a lower glass transition temperature and the existence of two hydroxyl ends groups that show the same reactivity.[7]

Based on these antecedents, and with the aim of studying new thermally crosslinkable ester oligomers, low molecular weight fractions of PMPPDT (hydroxytelechelic oligoesters) have been synthesized and characterized, and the functionalization of their hydroxy end groups with imide containing reagents has been attempted.

The experiments described in this article have also been oriented to compare the behavior of polyesters (polyterephthalates) of different glycols that, pre-

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sumably, may offer different alternatives as polymer models and as reactive oligomers. Therefore, a comparison between oligoesters of diethyleneglycol (DEG) and MPPD has been done.

EXPERIMENTAL

Materials

MPPD and dimethyl terephthalate (DMT) were purified by recrystallization from acetone/water = 1/2 and from methanol, respectively. Diethylene glycol (DEG) was distilled under reduced pressure. The 4-maleimido and the 4-nadimido benzoic acids and their corresponding acid chlorides were synthesized according to the procedure previously described.[1]

Synthesis of the Polyester Oligomers (PTMPPD)

Low molecular weight polyterephthalates were synthesized from DMT and MPPD by ester interchange. Three different MPPD/DMT molar ratios were used: 10/1, 4/1, and 2/1 to obtain hydroxytelechelic oligomers with different molecular weights ranging from 500 to 3100 ($\bar{X}_n$ = 1.3, 5, 8.5, 11). The synthetic method is illustrated with the following examples.

A mixture of 97.0 g (0.5 mol) of DMT, 146.0 g (1.1 mol) of MPPD, and 0.2 g of isopropyl titanate (0.2% w/w DMT) was heated with continuous stirring under nitrogen at 190°C for 2 h and then an additional 2 h at 200°C until the evolution of methanol ceased.

After that, the temperature was raised to 220°C and a vacuum of less than 1 mbar was applied to remove the MPPD in excess. The reaction was monitored by ^{1}H-NMR and GPC to control the molecular weight of the oligomer.

The final reaction product was poured into cold methanol. Two fractions were separated: one was soluble and contained the lower molecular weight oligomers, and the other, insoluble in methanol, contained the higher molecular weight species.

Further purification was performed by extraction with *n*-hexane in a soxhlet apparatus to eliminate the methylester terminated oligomers that remained in the mixture due to the low reactivity of MPPD, as will be shown later. The $\bar{X}_n$ of both fractions was 5.0 and 11.5.

By this method a molar ratio 10/1 was used to obtain the bis(2-methyl-2-propyl-3-hydroxypropyl) terephthalate ($\bar{X}_n$ = 1) as the main reaction product. After heating to 200°C for 4 h no more methanol distilled, and the reaction mixture was poured into hot water to separate the product from the glycol that remained in solution. However, even after several washings, there was some glycol that could not be eliminated. So, in order to remove it entirely, the mixture was heated at 150°C under vacuum (0.1 mbar), thus allowing the distillation of the glycol without postcondensation because the catalyst used in this case (zinc acetate) was soluble in water.

After this treatment, a mixture of hydroxyl-terminated oligomers with $\bar{X}_n$ = 1.3 was obtained.

Comparative Transesterification Reactions of DEG and MPPD with DMT

Two parallel reactions were performed to compare the relative reactivities of DEG and MPPD versus DMT. In both reactions the ratio DMT/glycol was 1/2, and isopropyl titanate (0.2% w/w DMT) was used as catalyst. An initial temperature of 160°C was maintained for 2 h. Then the temperature was increased to 180°C for 1 h and to 190°C for 8 h. No vacuum was applied during the reactions that were monitored by GPC to compare the polymerization progress in both cases.

Oligomers End-Capping

The modification with nadimide groups was carried out by reacting the hydroxyl end groups with an excess (15–50%) of 4-nadimidobenzoyl chloride in chloroform solution, with triethylamine as an acid acceptor and *N,N*-dimethyl-4-aminopyridine as catalyst. The use of this latter allowed the reaction to proceed approximately ten times faster and with better yields than in the absence of catalyst.

An example of this type of reaction, for the modification of the oligomer of $\bar{X}_n = 8$ follows: 8.000 g (0.0035 mol) of PTMPPD, 1.45 mL (0.01 mol) of TEA, and 0.13 g (0.1 mol/mol acid chloride) of *N,N*-dimethyl-4-aminopyridine were dissolved in 50 mL of dry chloroform at room temperature under a nitrogen atmosphere. In one-half hour, 3.140 g (0.010 mol) of 4-nadimidobenzoyl chloride were added portionwise to this solution with continuous stirring. The reaction was controlled by GPC, and it was stopped when modification was complete, after 7 h in this case. The solution was then poured into cold methanol, and the nadimide end-capped oligoester was isolated as a white precipitate.

The modification with maleimides was unsuccessful by this general route giving way to crosslinked systems in all cases.

Characterization

Gel permeation chromatography (GPC) was performed with a Waters M510 pump using chloroform as solvent. The columns were PLgel (Polymer Laboratories) with pore sizes of 100, 500, and 1000 Å. The flow rate was 1.0 mL/min. Detection was accomplished with a Waters R401 differential refractometer and a Philips PU4025 UV detector (variable wavelength).

Using TMS as internal standard and $CDCl_3$ as solvent, ^1H and ^{13}C nuclear magnetic resonance spectra were taken on a Bruker AM-200, 200 and 50 MHz, respectively.

Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC4 attached to a 3600 data station at a heating rate of 20°C/min under nitrogen atmosphere, using powdered samples weighing 8 ± 1 mg.

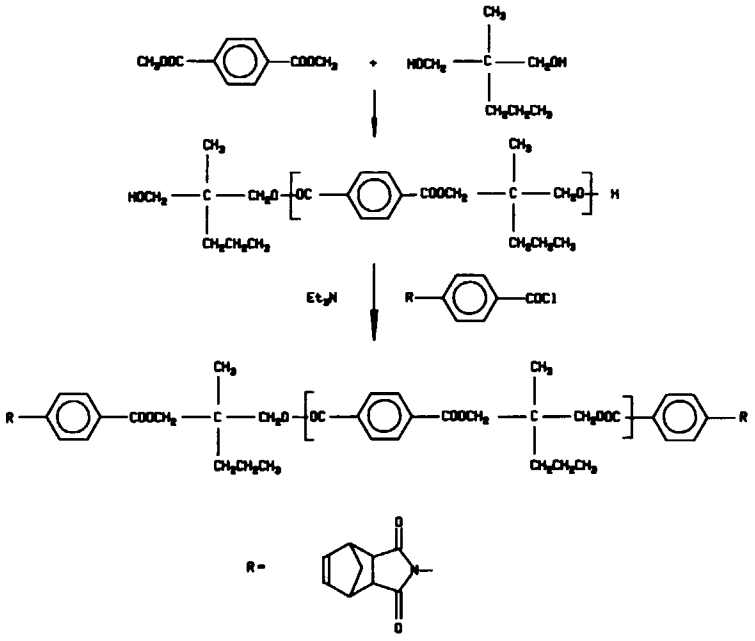
Vapor pressure osmometry (VPO) was performed on a Knauer osmometer in chloroform solutions at 37°C.

Thermogravimetric analyses (TGA) were obtained on a Perkin-Elmer TGS-2 device under nitrogen flow at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Oligomers Synthesis

Imide end-capped oligomers were synthesized in two steps according to Scheme 1.



Hydroxytelechelic Poly(2-methyl-2-propyl-1,3-propylene-terephthalate)

Hydroxytelechelic oligoesters with $\bar{M}_n$ = 510, 1000, 1500, 2250, and 3100 were obtained by transesterification from DMT and MPPD in excess. The different oligomers were obtained by using stoichiometric imbalance and by quenching the reaction at the correct time according to the analytical data given by GPC. Fractionated precipitation techniques were also used to accomplish the final separation of the oligomers. The characterization of the oligomers is shown in Table I.

It must be remarked that the low reactivity of the MPPD forced the use of long reaction times and high temperatures in the first step of the transesterification to avoid the presence of unreactive methoxycarbonyl end groups in the final products.

The presence of this kind of ends could be easily controlled by GPC and ^{1}H-NMR. In Figure 1 several GPC chromatograms taken at different stages of the reaction are shown. The assignment of the peaks was confirmed by comparison of the relative intensities of the peaks as a function of the stoichiometric ratio DMT/MPPD (1/1, 1/2, · · ·).

A comparative study of the transesterification reaction of DMT with MPPD and DEG with a stoichiometric ratio DMT/glycol = 1/2 clearly shows the indicated low reactivity of MPPD.

TABLE I
Characterization of the Series of Unmodified Oligomers[a]

Sample	$\bar{M}_n$[a] VPO	$\bar{X}_n$ ^{1}H-NMR	V_r[b] GPC	T_g (°C) DSC	Weight loss TGA
1	510 (1.3)	1.4	22.5 (m) (1.2) 21.3 (d)	−24	48
2	900 (2.9)	2.7	20.4 (t) (3.0)	4	34
3	1450 (5.0)	5.0	19.9 (te) (4.6) 19.5 (pe)	29	19
4	2250 (8.2)	8.1	18.3 (7.9)	42	14
5	3100 (11.2)	11.5	17.4 (11.0)	45	10

[a] The values of $\bar{X}_n$ are given in parentheses.
[b] m: monomer, d: dimer, t: trimer, te: tetramer, pe: pentamer.

In Figure 2 the evolution of the $\bar{X}_n$ is shown in both cases, determined by GPC, as a function of the reaction times.

Whereas $\bar{X}_n$ rapidly increases in the case of DEG approaching the equilibrium value for this stoichiometric imbalance ($\bar{X}_n = 3$), in the case of MPPD the increase of $\bar{X}_n$ is much slower. Moreover, to obtain a $\bar{X}_n = 1$, 5 h were necessary for MPPD, against 30 min for DEG.

Modified Oligomers

The reaction of the hydroxyl chain ends with acid chlorides bearing maleimido and nadimido groups has been proved as a very suitable approach to obtain this kind of oligomers.[1,8]

Consequently, the modification of the polyesters was first attempted by this method. However, the much lower reactivity of the hydroxyl groups in this case made the modification very difficult, and virtually no modification was achieved in most cases.

In the case of the nadimido groups, even under strengthed conditions (75% excess of acid chloride and reaction times up to 100 h, $T = 60°C$), high conversions could not be achieved. It was found by GPC that very long times were necessary to esterify the hydroxyl in both chain ends, the monofunctionalized oligomers being the intermediate products as it was confirmed by ^{1}H-NMR. The final products obtained this way showed modification degrees between 75 and 90%, depending on the molecular weight of the oligomers.

Although other systems were tried (dioxane/pyridine instead of chloroform/triethylamine) in order to increase the reaction temperature, the results could not be improved.

Better results were achieved by using *N,N*-dimethyl-4-aminopyridine as acylation catalyst, which has been used with increasing regularity[9] due to its exceptional catalytic effect.

The use of 0.1 mol of catalyst per mol of acid chloride allowed the reaction to be complete in reasonable time (5–10 h), at room temperature, and led to fully modified oligomers.

After optimization of the reaction conditions in the case of a simple model (Nad–MPPD–Nad), three oligomers with $\bar{X}_n$ = 1.3, 3, and 8 were modified

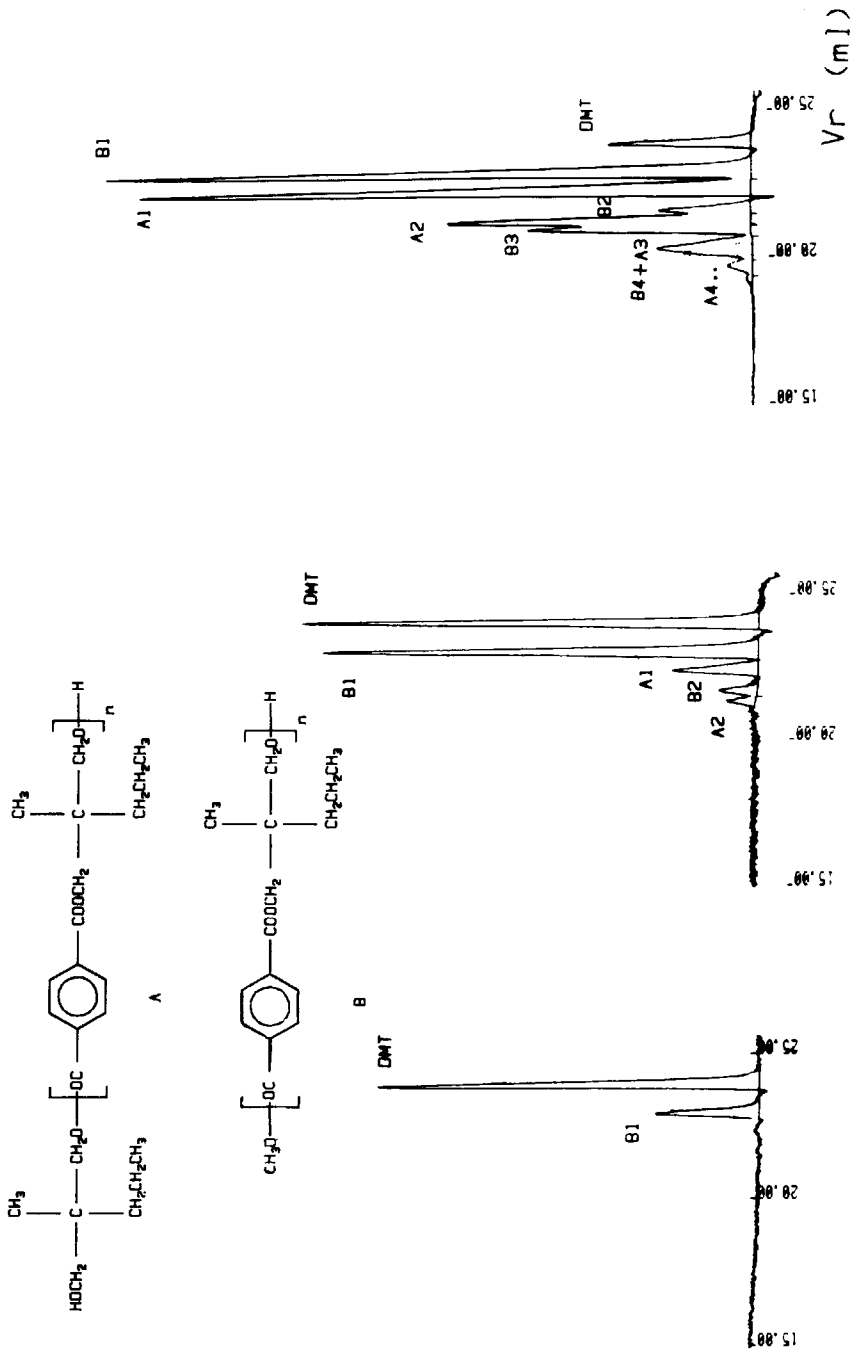


Fig. 1. Gel permeation chromatograms of the reaction mixture at different stages of the first step (no vacuum applied) of the transesterification reaction between DMT/MPPD : 1/2. The figures refer to the value of n.

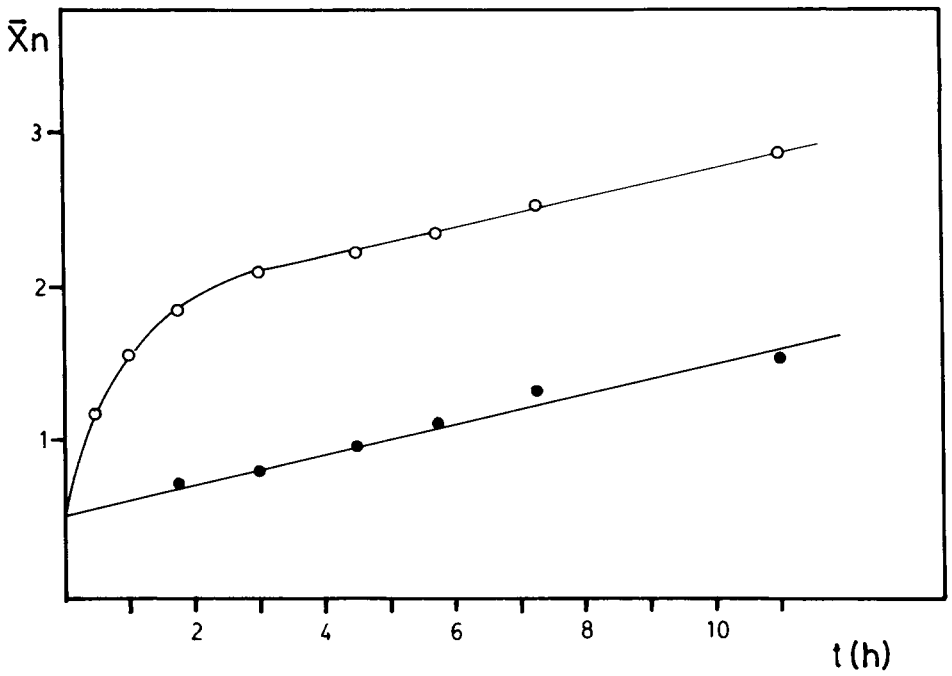


Fig. 2. Evolution of the polymerization degree ($\bar{X}_n$) versus the reaction time for the transesterification of DMT/DEG : 1/2 (○) and DMT/MPPD : 1/2 (●).

with the aim of studying the effect of the molecular weight in the modification reaction and in the properties of the modified oligomers.

The two lower molecular weight oligomers were chosen because the effect of the molecular weight in reticulated networks is more important in the region of low molecular weights and vanishes when it increases.[10]

In this way the modified oligomers shown in Table II could be obtained. Oligomers 1*N* and 4*N* were prepared directly from the corresponding hydroxyl terminated 1 and 4, while oligomers 2*N* and 3*N* were both obtained by modification of 2 and subsequent separation by fractionated precipitation. Their corresponding GPC chromatograms are shown in Figure 3.

TABLE II
Characterization of the Series of Nadimide End-capped Oligomers[a]

Sample	$\bar{X}_n$ ^{1}H-NMR	V_r[b] GPC	T_g (°C) DSC	Weight loss TGA
1*N*	1.06	20.5 (m) (1.3) 19.9 (d)	67	20
2*N*	2.2	19.5 (t) (2.3)	50	14
3*N*	3.0	19.1 (te) (3.2)	47	14
4*N*	7.5	18.1 (7.0)	65	10

[a] The values of $\bar{X}_n$ are given in parentheses.
[b] m: monomer, d: dimer, t: trimer, te: tetramer.

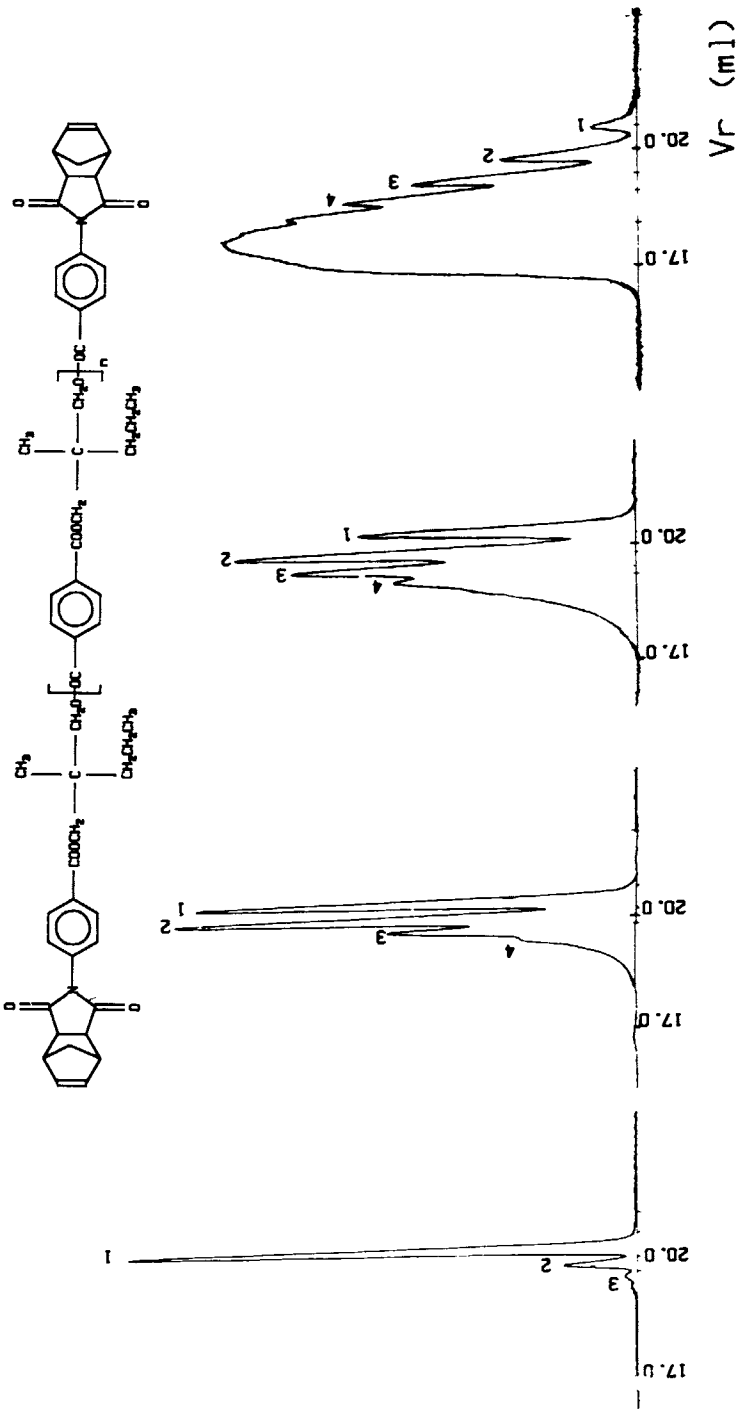


Fig. 3. Gel permeation chromatograms of the series of nadimide-modified oligomers. The figures refer to the value of n.

However, in the case of the modification with maleimido groups, this route was unsuccessful, always giving way to crosslinked products. The high reactivity of the double bond precludes the achievement of the esterification reaction in high yields if the crosslinking reaction is to be avoided. This is probably due to the fact that the tertiary amines used to catalyze the esterification also work as catalysts in the polymerization through the double bonds.[11]

GPC

The molecular weight of the oligomers was measured by GPC according to the formula

$$\bar{M}_n = \sum C_i / \sum (C_i/M_i)$$

M_i and C_i being the molecular weight and the concentration of the ith oligomer. In the case of lower molecular weight oligomers (up to $\bar{X}_n = 6$), the ability of the column set to give separate peaks for each oligomer allowed us the direct substitution in the formula.

However, when the molecular weight increases, the peaks collapse, giving a continuous distribution. This makes it necessary to use a calculation program in which values of $\bar{M}_n$ are attributed to the values of V_r taken at regular intervals. The correspondence between $\bar{M}_n$ and V_r is obtained from the calibration line built for the lower molecular weight oligomers that give separate peaks. Retention volumes for these oligomers are listed in Tables I and II.

The molecular weights determined by this method for the unmodified and nadimide-modified oligomers are in good agreement with those obtained by other methods (Tables I and II).

NMR

The 200-MHz ^{1}H-NMR corresponding to the unmodified oligomers with X_n = 1.2 and 5 are shown in Figure 4. The structure of these oligomers and the assignments of the peaks, made by a direct comparison of the spectra, are summarized in Table III.

As can be observed, the signals corresponding to the glycol moiety appear at different chemical shifts depending on their location, either at the end or in the middle of the chain. So if protons 2′, 3′, 4′, 5′, 6′ and 2, 3, 4, 5, 6 are compared, a shifting to a higher field is observed for the "end" protons except in the case of 5 and 5′ as could be expected.

This shifting would allow the quantitative determination of the proportion of "end" and "center" glycol and permit the direct determination of molecular weight. However, this determination is only possible for certain types of protons. Protons 2 are clearly separated from the other aliphatic signals, thus allowing a good determination of the ratio end to center by comparison with 2′ + 5 + 5′. Protons 5 + 5′ give way to a very distorted triplet centered at 0.88 ppm due not only to their coupling with protons 4 + 4′ but also to protons 2′, which appear at 0.90 ppm. That causes this signal to present different patterns as a function of the $\bar{M}_n$ of the oligomer.

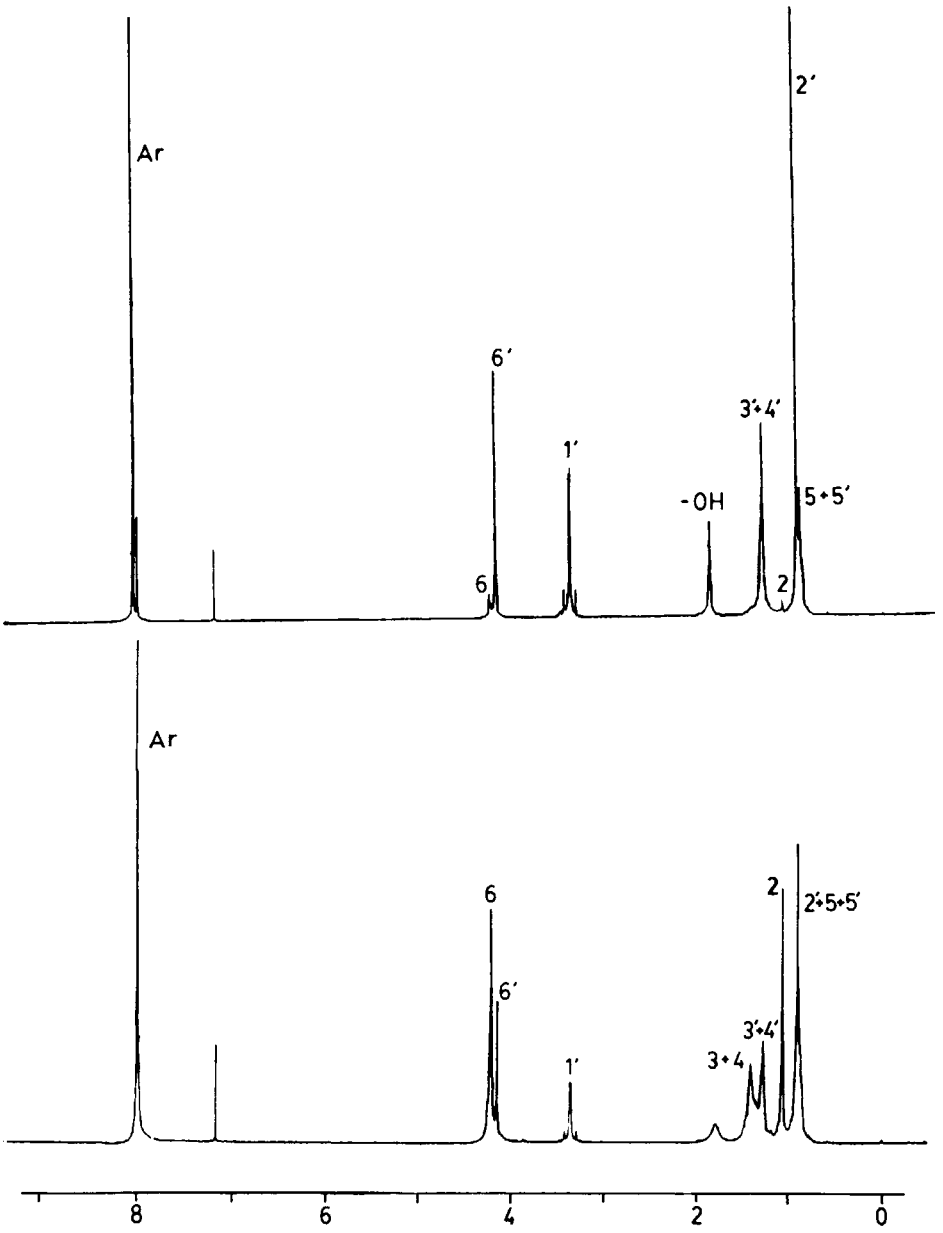
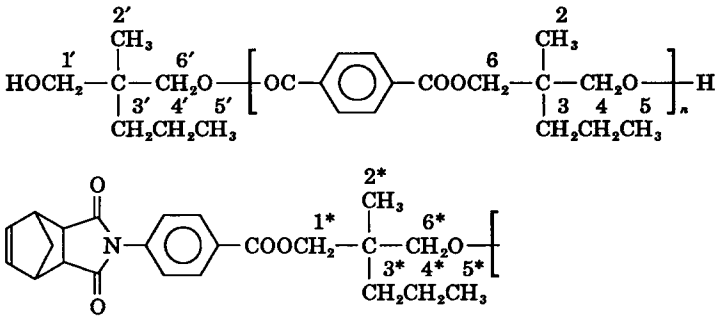


Fig. 4. 200-MHz ^{1}H-NMR spectra of unmodified oligomers with $\bar{X}_n$ = 1.4 and 5 (samples 1 and 3). For the assignments of peaks see Table III.

Protons 3 + 4 and 3′ + 4′ appear as a complex unresolved system that changes with the molecular weight.

More accurate determination of $\bar{X}_n$ can be made by comparison of the methylene protons linked to the ester group (6, 6′) with those of protons of the CH_2OH end groups (1′) that appear as an AB pattern due to the vicinity to an assymetric carbon.

TABLE III
^{1}H-NMR Chemical Shifts of the Different Types of Glycol Moieties



1′	3.37, 3.34			1*	4.2
2′	0.90	2	1.06	2*	1.04
3′, 4′	1.27[a]	3, 4	1.41[a]	3*, 4*	1.41[a]
5′	0.88	5	0.88	5*	0.88
6′	4.16	6	4.22	6*	4.22

[a] Complex pattern. The value corresponds to the maximum of the signal.

Furthermore, this is clearly the only type of end groups present in these polymers. No signal can be detected at 3.95 ppm, which confirms the absence of CH_3OOC end groups.

Aromatic rings are always joined to two ester groups independent of their position in the chain. This makes the differences much smaller than in the case of aliphatic protons. The difference between the protons corresponding to end and center is only 0.02 ppm (7.98 ppm for end and 8.00 for center). The aromatic rings joined to two end glycols give a peak at 8.02 ppm (see Fig. 4). These small differences do not allow any quantitative determination from these signals.

The esterification of the hydroxyl end groups gives the new signals corresponding to the nadimide ring and to the aromatic ring directly joined to the imidic nitrogen.[12,13] The assignments of the glycol protons are also included in Table III.

Although the disappearance of the signals at 0.90 and 4.16 ppm indicates the absence of hydroxyl end groups, only in the case of the peak at 4.16, which does not overlap, is it possible to follow this disappearance up to the completion of the reaction.

By comparison of the aromatic protons or the methylene protons (6 and 6′), with the protons of the double bond, the degree of polymerization of these oligomers could be accurately determined (Table II).

^{13}C-NMR was used to confirm the results obtained by ^{1}H-NMR. Figure 5 shows the spectrum of the unmodified oligomer ($\bar{X}_n = 11.5$) and the assignment of the peaks. As can be seen, the carbons corresponding to end and center glycols can be easily resolved in most cases. This assignment has been previously reported[3] for the carbons belonging to a center glycol. However, no mention was made of the end glycols. This can be attributed either to the low field used

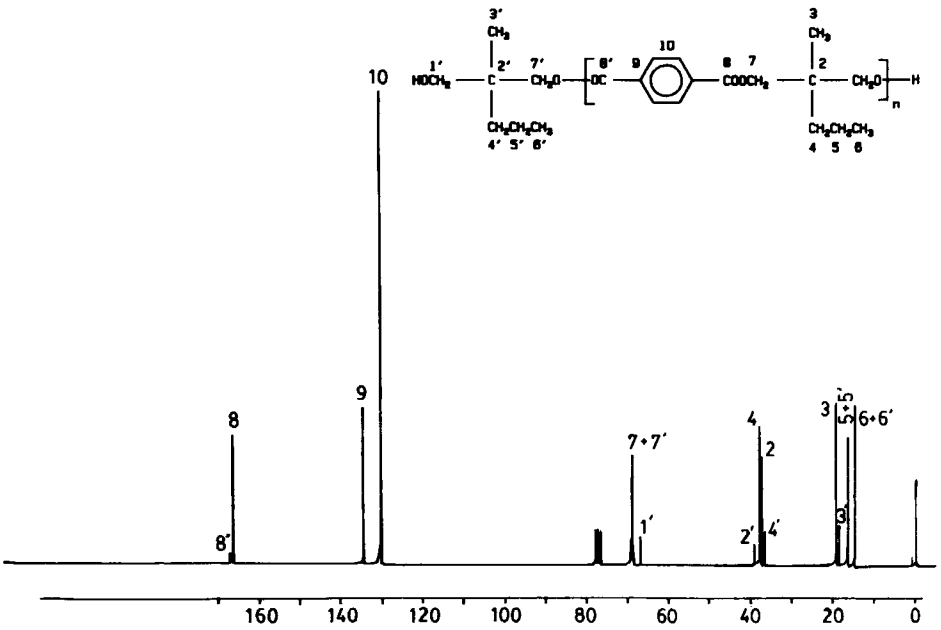


Fig. 5. 50-MHz ^{13}C-NMR spectrum of the unmodified oligomer with $\bar{X}_n$ = 11.5 (sample 5).

in that study (15 MHz) or to the higher molecular weight of the polymer synthesized in that case (no mention of the molecular weight appears in the publication).

The modification of the oligomers caused the disappearance of the signals corresponding to the end of chains (1′, 2′, 3′, 4′, 8′). The absence of these signals, as well as the appearance of the nadimide signals,[12,13] clearly indicates a very high degree of modification.

The intensities ratio between center and end carbons agrees with those obtained by ^{1}H-NMR.

DSC

The oligomers were studied by DSC in order to determine their thermal behavior. No melting transitions were found in any case, indicating that the oligomers did not crystallize under the conditions employed, contrary to those of DEG that crystallized from solution. Even after annealing they behaved as essentially amorphous.

The glass transition temperatures are listed in Tables I and II. As can be seen, the behavior of the unmodified oligomers is characteristic of a low molecular weight series, the T_g substantially increasing with the molecular weight. The introduction of the bulky nadimide groups gave way to an increase of T_g that depended on the relative influence of these groups. When the molecular weight increased, the influence of the end groups decreased and the modified oligomers behaved more like the unmodified ones (ΔT_g = T_g modified—T_g unmodified decreases).

As could be expected from a comparison of the structure of both glycols, the MPPD oligomers have a higher T_g than those of DEG (approximately 20°C

higher for the same degree of polymerization). The T_g increment due to the end capping with nadimide groups is similar in both cases.

All the modified oligomers gave a broad exotherm corresponding to thermal crosslinking through the double bond of the imide group (Fig. 6). The maxima of the exotherm occur at approximately 350°C. A previous endotherm, due to reverse Diels–Alder reaction with cyclopentadiene evolution can be observed.[14,15] The crosslinking of oligomers with nadimide end groups is a rather complex process that would deserve further experimentation.

TGA

The thermal stability was checked by dynamic TGA under a nitrogen atmosphere at a heating rate of 20°C/min. The weight losses at 400°C, summarized on Tables I and II, decreased with the increase in molecular weight in both types of oligomers. In the case of the unmodified oligomers, the weight loss is also caused by a simultaneous transesterification reaction with loss of MPPD and molecular weight increase, as it was tested by comparative GPC before and after the thermal treatment. This effect is more important in the lower molecular weight samples.

The weight loss was lower in the case of the nadimide modified oligomers due to the simultaneous crosslinking process and to the impossibility of the transesterification reactions. However, in these cases a first weight loss step due to the evolution of cyclopentadiene could be observed.

The same behavior had been observed for DEG terephthalates, no remarkable difference in the thermal resistance being noticeable.

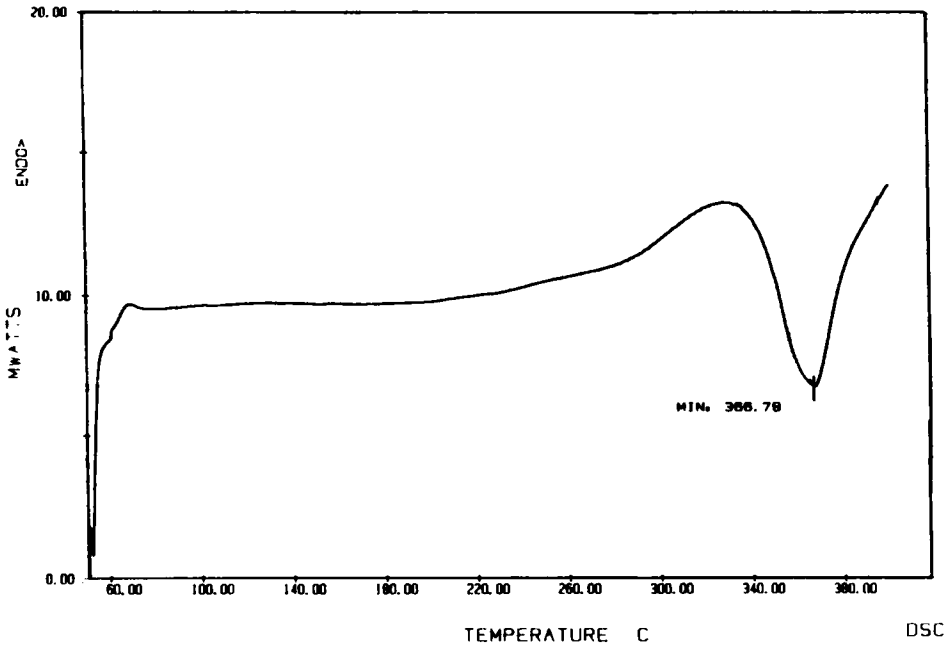


Fig. 6. DSC curve corresponding to the nadimide end-capped oligomer 1*N* (scanning rate: 20°C/min).

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