Synthesis and Characterization of Imide End-Capped Oligomers of Poly(diethyleneglycol Terephthalate)

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Synopsis

A series of imide end-capped oligoesters were prepared by reacting a number of hydroxyl-terminated poly(diethyleneglycol terephthalate) oligomers ($\overline{X}_n$ ranging from 1 to 20) with N-(4-chlorocarbonylphenyl)maleimide and N-(4-chlorocarbonylphenyl)nadimide. All the oligomers were characterized by vapor pressure osmometry, ^{1}H- and ^{13}C-NMR and GPC. The thermal properties were also investigated and a correlation of the thermal behavior with molecular weight and the type of reactive end groups was established. Molecular models were also synthesized and characterized to obtain reliable analytical data for the determination of the oligomers composition.

INTRODUCTION

Functionalization of polymers and oligomers has frequently been directed towards the attainment of crosslinkable polymers. One of the general approaches used for these purposes has been the endcapping of oligomers with reagents bearing polymerizable functional groups.[1,2]

When polyterephthalates are synthesized by the common ester interchange procedure from dimethylterephthalate (DMT) and glycols, excess glycol monomers are used, thus giving an hydroxyl-terminated polymer. These polyesters can be crosslinked with, for instance, a triisocyanate, to yield elastomers with outstanding properties.[3-6] They can also be easily functionalized through their hydroxyl ends. We have chosen poly(diethyleneglycol terephthalate) as one of the cheapest and more easily preparable polyesters. In addition, the polymer is soluble and uncrystallizable from the melt.

Because nadimide and maleimide end-capped oligomers are at present among the most important polymers for applications in advanced technologies,[7-9] the synthesis of maleimide- and nadimide-terminated oligoesters will be described in this work as well as their characterization by NMR, GPC, and DSC.

EXPERIMENTAL

Diethylene glycol (DEG) and dimethyl terephthalate (DMT) were purified by distillation at reduced pressure and recrystallization from methanol respectively.

The 4-maleimidobenzoic acid was synthesized by the usual Searle method[10] in two steps, the first one from maleic anhydride and 4-aminobenzoic acid and the second one by cyclodehydration of the maleamic acid precursor with acetic anhydride and sodium acetate. The product was recrystallized from ethanol–water; mp 227°C.

The 4-nadimidobenzoic acid was obtained in one step from nadic anhydride (5-norbornene-2,3-dicarboxylic acid anhydride) and 4-aminobenzoic acid in refluxing acetic acid. Recrystallized from ethanol–water gave an mp of 240°C.

The corresponding acid chlorides were synthesized by reacting both acids with excess of thionyl chloride in the usual way.[11] They were purified by recrystallization from n-heptane; mp = 175 and 155°C for maleimide and nadimide, respectively.

Synthesis of the Polyester Oligomers (PTDEG)

Polyester oligomers were synthesized from DMT and DEG (mol ratio 1/2, DMT/DEG) by ester interchange. Isopropyl titanate (0.2% w/w DMT) was used as the catalyst.

The mixture was heated to 175°C under N_2 until evolution of methanol ceased. After that, the temperature was raised to 200°C and the polycondensation proceeded by elimination of DEG. A vacuum of less than 1 mbar was applied up to the last stage of the reaction. The amount of collected DEG was monitored to control the molecular weight of the polymer. The final reaction product was dissolved in chloroform, filtered through Celite, and precipitated in methanol. The polymer was fractionated using chloroform/methanol as solvent/nonsolvent system. Several fractions were obtained with M_n ranging between 2000 and 4500.

Synthesis of Very Low Molecular Weight Oligomers

Two oligomers with $\overline{X}_n = 1.05$ and 2.6 were obtained in the same way by using a molar ratio DEG/DMT = 6/1. Once the theoretical amount of methanol was released, the temperature was lowered to 100°C in order to stop the condensation reaction, and the excess of DEG was distilled at 70°C under reduced pressure. The reaction mixture was analyzed by GPC and ^{1}H-NMR to control the molecular weight increase. The reaction product with $\overline{X}_n = 1.6$ and free DEG (11% w/w) was poured into cold water. The white precipitate was filtered and the water was removed from the solution (rotary evaporation). The precipitate is a mixture of oligomers with $\overline{X}_n = 2.6$, no traces of DEG being observed by NMR. The fraction that did not precipitate was purified by passing it through a column of Silicagel 60 (Merck A.G.) (50 g silica/g product) using ethyl acetate/acetone = 1/1 as eluent. A product with $\overline{X}_n = 1.05$, with no traces of DEG, was separated.

Oligomers End-Capping

The modification of the oligomers was carried out by reacting the hydroxyl end groups with an excess (15–50%) of 4-maleimido or 4-nadimidobenzoyl chloride in chloroform solution, with triethylamine as an acid aceptor. All the

reactions were followed by GPC. As an example, the modification reaction of the oligomer with $\overline{M}_n = 2000$ is given below.

The oligomer [6.000 g (0.003 mol)] and TEA [1.26 mL (0.0090 mol)] were dissolved in 40 mL of dry chloroform. Solid 4-maleimido benzoyl chloride [2.110 g (0.0090 mol)] was added portionwise to the stirred solution. The reaction proceeded under nitrogen for 5 h at 20°C and for an additional hour at 60°C to assure the complete modification of the end groups.

The solution was poured into cold methanol and the precipitate was filtered, washed with methanol, and dried under vacuum. Yield 86%; mp = 74°C.

The methanol used in the first precipitation was evaporated to recover the soluble parts in order to check the existence of side products in the reaction.

Synthesis of Model Compounds

Maleimide and nadimide end-capped DEG were obtained by esterification of DEG with 4-maleimido and 4-nadimido benzoyl chlorides in chloroform solution as previously described for the oligomers. They were crystallized from ethanol and methanol, respectively, giving melting points of 130°C for Mal–DEG–Mal and 97°C for Nad–DEG–Nad.

CHARACTERIZATION

Gel permeation chromatography (GPC) was performed with a Waters pump M510 using chloroform as solvent. The columns were PL gel (Polymer Laboratories) with pore sizes of 500 and 100 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).

^{1}H- and ^{13}C-nuclear magnetic resonance spectra were recorded on a Bruker AM-200, 200 and 50 MHz, respectively, and a Bruker WM-360, 360 MHz for ^{1}H, using TMS as internal standard and $CDCl_3$ as solvent.

Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC-4 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 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.

Synthesis of Hydroxytelechelic Oligomers

In the first step the ester interchange method was used to obtain a low-molecular-weight polymer with hydroxyl groups in both ends. After fractionation, a series of suitable oligomers were obtained, which molecular

Scheme 1
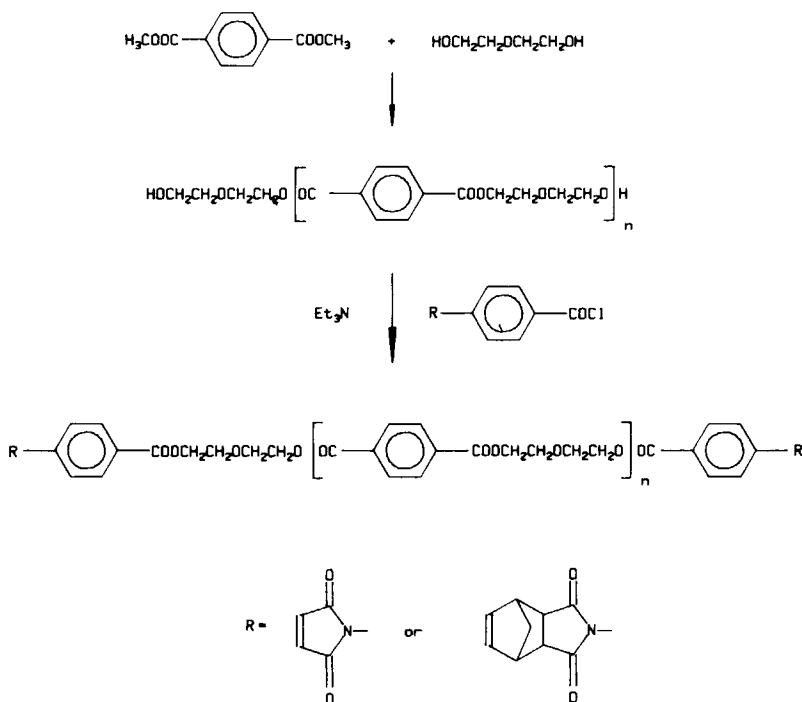
weights were determined by VPO and ^{1}H-NMR. The results of these determinations are shown in Table I, along with the elution volumes determined by GPC.

In order to obtain very low-molecular-weight oligomers, DMT was made to react with an excess of DEG (6/1 mol). This method has been previously used to prepare the corresponding monomer in the case of ethylene glycol (BHET)[12] and butylene glycol (BHBT).[13] However, in our case, the low melting temperature of the monomer and the low crystallizability of DEG terephthalates makes the separation more difficult.

As BHDET and DEG cannot be separated from each other by differences of solubility, it was necessary to eliminate most of DEG excess by vacuum distillation at the lowest temperature possible to reduce the condensation to a minimum during this process. This step was controlled by GPC and ^{1}H-NMR, to simultaneously monitor the progress of the condensation and the amount of remaining DEG.

This information is shown in Figure 1, illustrating the aliphatic region of the ^{1}H-NMR spectrum of the reaction at an intermediate step during this process.

Accordingly, we used the following relationships:

$$A\left(4H\left(\overline{X}_n - 1\right) + 4H\right) = \text{area 1}$$

$$B(8H) + A\left(4H\left(\overline{X}_n - 1\right) + 4H + 8H\right) = \text{area 2}$$

TABLE I
Molecular Weights Determined by VPO, ^{1}H-NMR, and GPC of the Series of Unmodified and Modified Oligomers

Sample	Unmodified			Maleimide		Nadimide	
	$\bar{M}_n^a$, VPO	$\bar{X}_n$, ^{1}H-NMR	GPC, V_r^a	$\bar{X}_n$, ^{1}H-NMR	GPC, V_r^a	$\bar{X}_n$, ^{1}H-NMR	GPC, V_r^a
1	350(1.0)	1.04	14.1(m)^b (1.05) 13.5(d)^b	1.3	13.2(m)^b (1.13) 12.7(d)^b	1.1	12.86(m)^b (1.13) 12.47(d)^b
2	720(2.6)	3.0	12.9(t)^b (2.4) 12.5(te)^b	3.5	12.4(t)^b (2.7) 12.2(te)^b	3.1	12.20(t)^b (2.4) 11.90(te)^b
3	2000(8.0)	8.0	11.45	9.0	11.35	10.5	11.48
4	2600(10.5)	11.5	10.85	15.5	10.92	14	10.91
5	3200(13.0)	15.0	10.5	20	10.60	18	10.56
6	4500(18.5)	20.0	10.2	33	10.26	30	10.19

^{a} The values of $\bar{X}_n$ are given in parentheses.
^{b} m = monomer, d = dimer, t = trimer, te = tetramer.
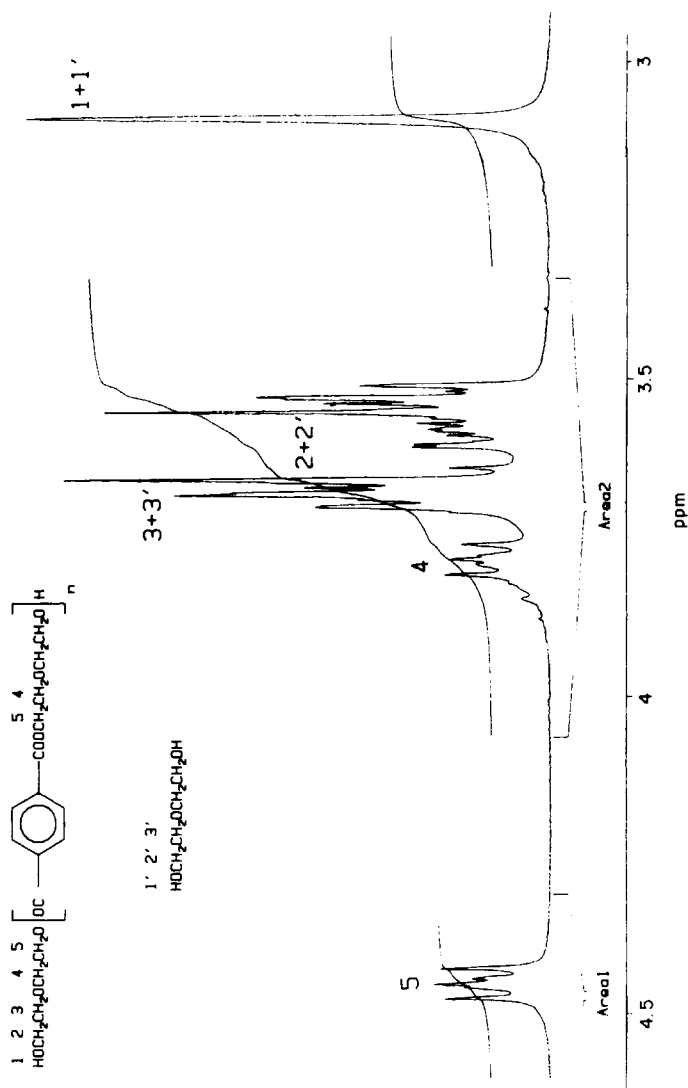
Fig. 1. ¹H-NMR spectrum of the aliphatic region corresponding to an intermediate step during the reaction between DMT and DEG (1/6).
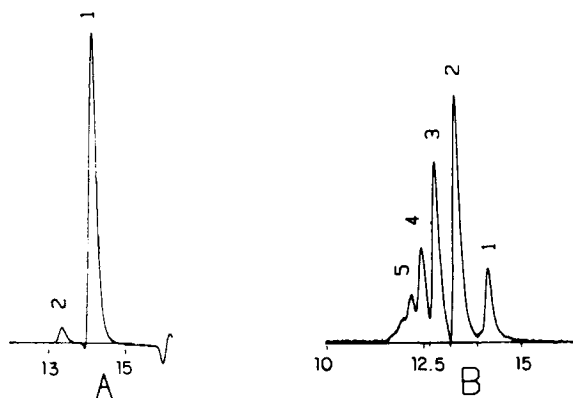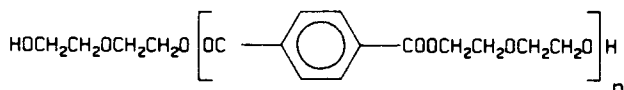
$$HOCH_2CH_2OCH_2CH_2O \left[OC \underset{}{\bigcirc} COOCH_2CH_2OCH_2CH_2O \right]_n H$$

Fig. 2. Gel permeation chromatograms of poly(diethyleneglycol terephthalate) oligomers of $\overline{X}_n = 1.05$ (A) and $\overline{X}_n = 2.6$ (B). The peak numbers correspond to the value of n. Retention volume is in mL.

H is the area corresponding to one proton in each particular spectrum: areas 1 and 2 are indicated in the figure. From these equations and the value of $\overline{X}_n$ determined by GPC (see below) we can calculate A and B, the molar fractions of oligomer and free DEG.

The distillation was stopped at $\overline{X}_n = 1.6$ and 40% of DEG (in mol) (11% w/w) as a compromise between the maximum amount of monomer and the minimum of free DEG.

Precipitation in cold water was a good method to separate BHDET (that remains soluble) from higher molecular weight oligomers. In that way, we obtained two fractions with $\overline{X}_n = 1.1$ and 2.6, respectively. The first fraction was purified by column chromatography obtaining BHDET of $\overline{X}_n = 1.05$ with no traces of DEG. GPC chromatograms of both oligomers are shown in Figure 2.

Oligomers End-Capping

To modify the hydroxyl ends of the oligomers, we chose the reaction with acyl chloride attached to maleimide or nadimide groups. The esterification reaction from acyl chlorides is recognized as rapid and quantitative and takes place at low temperature,[14,15] thus preserving the double bonds. Although the esterification by phase-transfer catalyzed reactions with crown ethers appeared as a promising method,[16,17] it gave crosslinked polymers in our case. In spite of the inconveniences of using acyl chlorides (the presence of a stoichiometric amount of tertiary amine makes possible the opening of the imide

groups in the presence of small amounts of water), this method has been found to be the most suitable for our purposes.

However, it was necessary to use an excess of acyl chloride (ranging from 10 to 50%) as a function of the molecular weight of the oligomers to obtain high degrees of modification (higher than 90% in all cases). This stoichiometric imbalance has been used in similar cases.[18]

The final products were characterized by ^{1}H- and ^{13}C-NMR in all cases to determine the extension of the modification. The results of these reactions are shown in Table I.

Special attention was paid to the monitoring of the reactions by GPC in the case of low-molecular-weight oligomers. The GPC revealed that the modification took place and was essentially complete within 1 h, but longer reaction times were necessary to achieve the modification of the last few hydroxyl groups, which in turn can favor the appearance of side products due to excess acyl chloride.

GPC

In Table I the retention volumes V_r corresponding to all the oligomers are shown.

A linear correlation could be established between the molecular weights (log M_n) determined by vapor pressure osmometry and the retention volumes at the maximum of the peak of the unmodified PTDEG oligomers.

Furthermore, the ability of the used column set to give separate peaks for the oligomers with $\overline{X}_n$ ranging from 1 to 5, allowed us to calculate the $\overline{M}_n$ of the lowest oligomers (1 and 2 in Table I), by using $\overline{M}_n = \Sigma C_i / \Sigma(C_i/M_i)$, M_i and C_i being the molecular weight and the concentration of the ith oligomer.

Although refractive index and molecular weight were assumed to be independent in this low-molecular-weight region, the results obtained in this way were in accordance with those of NMR or VPO. Furthermore, the retention volumes of these single peaks fit in the line determined previously.

The difference in retention volumes between unmodified and imide-modified oligomers decreased as $\overline{X}_n$ increased and became zero when $\overline{X}_n = 6$. Thus, in the case of imide end-capped oligomers, we have not measured the $\overline{X}_n$ by VPO, except in a few cases, and we have considered the V_r values as a useful parameter to determine molecular weights.

NMR

NMR was used as a main technique to study the structure and the type of chain ends in both the unmodified and the modified oligomers. Assignments for the various resonance peaks were made by comparison with model compounds and monomers.

In Figure 3 the 200 MHz ^{1}H-spectra of oligomer 3 ($\overline{M}_n = 2000$) with hydroxyl or maleimide ends, along with the assignments corresponding to each type of proton are shown. As can be seen in the first spectrum, the hydroxyl-chain ends can be clearly distinguished from the signals of the repeating unit in the regions of aromatic and aliphatic protons, due to the appearance of separate peaks in both of them.
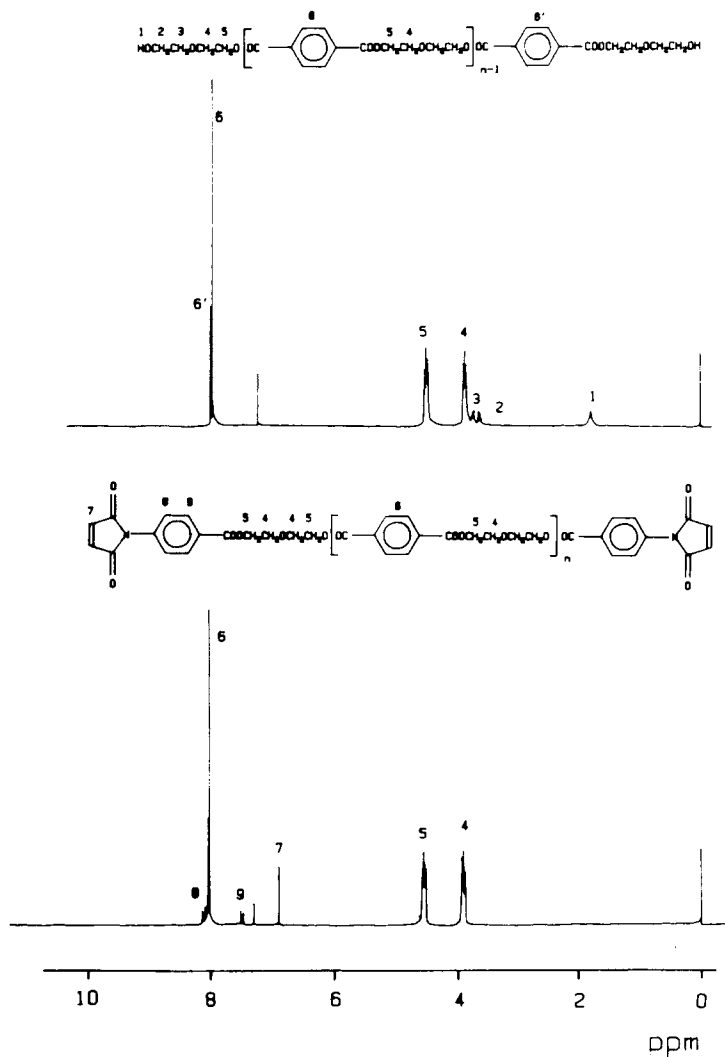
Fig. 3. ^{1}H-NMR spectra of oligomer 3 unmodified and maleimide end-capped.

Aliphatic protons give two different groups of signals, regardless of the molecular weight, one corresponding to chain protons (3.88 and 4.50 ppm) and another to end units (3.67 and 3.75 ppm). However, the aromatic region gives different patterns depending on the molecular weight. The oligomer 1, with $\overline{X}_n = 1.05$ shows two peaks, one of very high intensity at 8.1 ppm, due to aromatic rings between two DEG units with hydroxyl ends and a very small one at 8.05 ppm corresponding to the small amount of dimer. Oligomer 2, with $\overline{X}_n = 2.6$, presents a more complicated pattern, with peaks at 8.1 (very small), 8.06 and 8.05 ppm, attributed to inner and outer protons in a ring close to a chain end (predominant peaks), and 8.02 ppm, due to aromatic protons in the middle of the chain. The larger molecular weight oligomers show in all cases peaks corresponding to the middle and the end of chains (8.02 and 8.05 ppm).

The identification of these signals led us to the determination of $\bar{X}_n$ in all cases by comparison of end and chain protons.

As is evident, the relative intensity of the chain ends decreases as the molecular weight increases, thus making the determination of $\bar{X}_n$ with high accuracy difficult.

The esterification of the hydroxyl ends causes the disappearance of the signals at 3.67 and 3.75 and the appearance of the new signals from the double bonds of the maleimide (6.87 ppm) and the aromatic ring directly attached to the imidic nitrogen (AA'BB' system, 7.46 and 8.10 ppm). The aromatic protons of the modified oligomers also give way to separate peaks depending on whether they are located within the chain (8.03 ppm) or near the end of the chain (8.04 ppm) (Fig. 3).

The disappearance of the protons corresponding to unmodified hydroxyl ends is almost complete in every case, thus indicating a nearly quantitative modification.

When the unmodified end groups were detected by NMR, the following equations were used to calculate the molecular weight:

$$\left(4H\bar{X}_n + 4H\right)A + \left(4H\bar{X}_n + 8H\right)B = \text{area 1}$$

$$4HA = \text{area 2}$$

$$\left(4H\bar{X}_n + 4H\right)A + 4H\bar{X}_n B = \text{area 3}$$

A and B are the molar fractions of imide and hydroxyl terminated oligomers, respectively; area 1 is the area from 3.5 to 4.2 ppm, area 2 is from 6.6 to 7.0 ppm or from 7.35 to 7.55 ppm, area 3 is from 4.2 to 4.8 or from 7.7 to 8.4 ppm (see spectrum), and $\bar{X}_n$ is the number-average degree of polymerization. However, the detection and quantification of these remaining protons becomes difficult as the molecular weight increases, due to overlapping with other aliphatic protons and their very low relative intensities.

To gain insight into the quantitative determination of the end groups, several spectra were performed at higher field (360 MHz) with a flip angle of 45° and a delay time between pulses of 10 s to prevent the appearance of saturation effects. 32K of memory were used for the acquisition of the free induction decay (FID).

Even under these conditions, no significant improvement was achieved, as can be seen in Figure 4, where the spectrum of the oligomer 4 is presented. The measurements of $\bar{X}_n$ for higher molecular weight and highly modified oligomers are inaccurate due to the indicated overlapping of the very small signals. These correspond to the unmodified groups, which do not allow for the independent determination of their contribution.

In the case of nadimide-modified oligomers, the behavior is similar to that observed for maleimides. In this case new signals appear in the spectra corresponding to the nadimide ring.

^{13}C-NMR was used to support previous conclusions obtained by ^{1}H-NMR. In Figure 5 the ^{13}C-spectra of oligomer 4 unmodified and nadimide end-capped are shown.
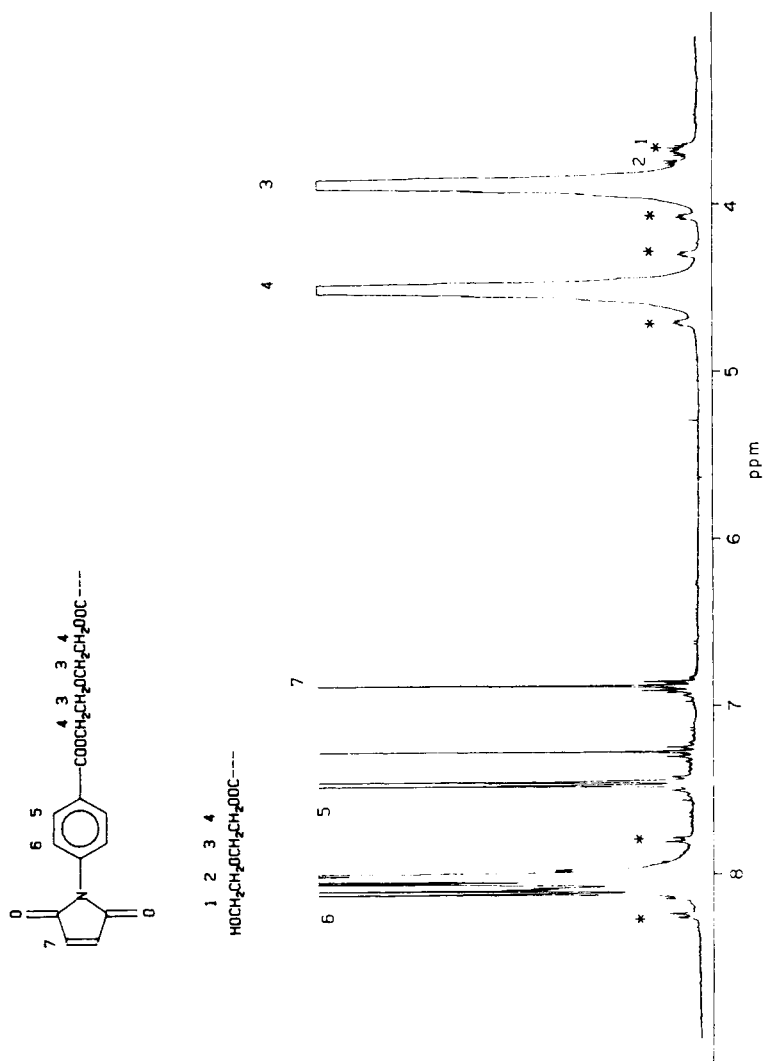
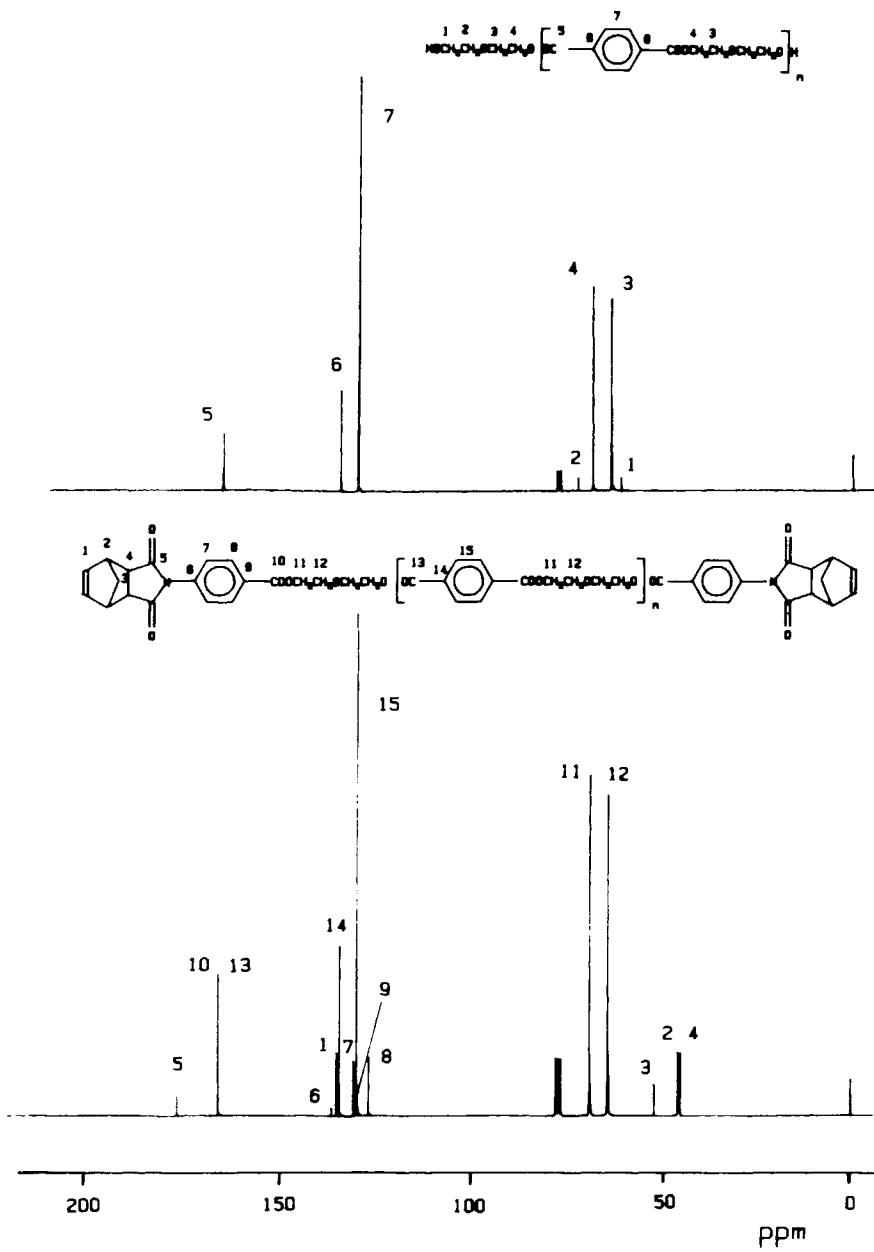Fig. 4. 360 MHz ^{1}H-NMR spectrum of oligomer 4 modified with maleimide.* ^{13}C satellites.

Fig. 5. ^{13}C-NMR spectra of oligomer 4 unmodified and nadimide end-capped.

TABLE II
Thermal characteristics of the Series of Unmodified and Modified Oligomers

	Unmodified			Maleimide				Nadimide			
Sample	T_m (°C)	T_g (°C)	Weight loss[a] (%)	T_m (°C)	T_g (°C)	ΔT_g	Weight loss[a] (%)	T_m (°C)	T_g (°C)	ΔT_g	Weight loss[a] (%)
1	43	−46	70	125	33	79	15	91	48	94	21
2	44	−24	27	—	24	48	16	—	33	57	22
3	75	8	24	74	26	18	15	78	33	25	18
4	92	14	20	77	27	13	16	78	32	18	18
5	89	19	18	74	24	5	13	74	26	7	15
6	89	20	16	77	24	4	12	74	26	6	15

[a]At 400°C.

The absence of the signals at 61.7 and 72.5 ppm in the modified oligomer indicates a very high degree of modification, the remaining unmodified groups being under the limit of detection of this technique. The intensities ratio between chain and end carbons agrees with those obtained by ^{1}H-NMR.

Thermal Characterization

Melting points and glass-transition temperatures obtained by DSC are summarized in Table II. All the oligomers were crystalline except those of $\overline{X}_n = 2.6$ modified with maleimide and nadimide which were unable to be crystallized by any means, probably due to their molecular weight heterogeneity. However, no oligomer crystallized from the melt so that glass transitions could be observed in a second run after cooling.

Glass transition temperatures of unmodified oligomers increased initially with increasing molecular weight and then reached an asymptotic value. However, when modified, the trend is reversed and the oligomers with lower molecular weight gave the higher T_g, due to the effect of the end groups. When the relative influence of the imide groups decreases, the T_g decreases approaching the value of the unmodified oligomers. Values of T_g are listed in Table II.

The influence of the imide rings can be clearly observed by the fact that the model compounds Mal–DEG–Mal and Nad–DEG–Nad display the highest T_g's, at 40 and 52°C, respectively. The T_g's of nadimide-modified oligomers are higher than those of maleimide end-capped, as could be expected from the structure of both imides.

All the modified oligomers gave a broad exotherm, corresponding to thermal crosslinking through the double bonds of the imide groups. The maxima of the crosslinking exotherm occurs at approximately 290°C in the case of maleimides and 350°C for nadimides. In the nadimide oligomers, a previous endotherm corresponding to reverse Diels–Alder reaction with cyclopentadiene evolution can be observed.[19,20] The crosslinking is being studied at present and the results will appear in a future publication.

The thermal stability has been checked by TGA under an N_2 atmosphere at a heating rate of 20°C/min. The percentages of weight loss after a treatment up to 400°C are shown in Table II.

The 5% weight losses are approximately attained at 350°C for the unmodified and at 390°C for the maleimide oligomers. The nadimide end-capped oligomers show a weight loss at lower temperature (240°C) due to the evolution of cyclopentadiene after the reverse Diels–Alder reaction. Because the relative amount of end-capping groups depends on the molecular weight, the influence of this first step decreases with the molecular weight.

The results of Table II indicate that end-capping causes a decrease of weight loss at 400°C, as a consequence of simultaneous crosslinking. This effect is more clearly observed in the lower molecular weight samples. The weight losses are greater in nadimides due to the elimination of cyclopentadiene and less crosslinking.

CONCLUSIONS

Imide-terminated oligomers of poly(diethyleneglicol terephthalate) can be prepared in virtually quantitative yields by condensation of hydroxy-terminated fractions of PDET with imide-containing reactants such as 4-chlorocarbonylphenylmaleimide and 4-chlorocarbonylphenyl nadimide.

The course of the functionalization reaction can be followed by ^{1}H-NMR and ^{13}C-NMR spectroscopy as well as by GPC. Both methods indicate a high degree of modification, that may be up to 100% for the lower molecular weight oligomers.

The end-capping of terminal groups has permitted the attainment of new flexible bismaleimides and bisnadimides. The introduction of the imide end groups brings about the inversion in the trend of T_g with respect to the unmodified oligomers, so that the lower the $\overline{M}_n$ the higher the T_g of the modified PDET oligomers. However, the influence on the melting points is much less and only slight differences are observed between modified and unmodified oligomers, except in the case of oligomer 1. Moreover, the functionalization by means of imide end-capping causes the oligomers to be crosslinkable by simply heating and improves the thermal resistance of these materials.

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