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Synthesis and characterization of α,ω-hydroxy and nitrato telechelic oligomers of 3,3-(nitratomethyl) methyl oxetane (NIMMO) and glycidyl nitrate (GLYN)

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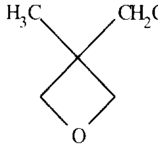
The synthesis of α,ω-hydroxy telechelic, low-molecular-weight oligomers (degree of polymerization of less than 10) of glycidyl nitrate (GLYN) and 3,3-(nitratomethyl) methyl oxetane (NIMMO) by the activated monomer mechanism is described. Difunctional and/or trifunctional compounds may be prepared. The end-nitration of these compounds has been investigated using dinitrogen pentoxide in dichloromethane to form α,ω-nitrato telechelic oligomers. The materials were characterized by size exclusion chromatography, infrared and nuclear magnetic resonance spectroscopies. Differential scanning calorimetry was used to study the thermal properties of the compounds as they are envisaged to be energetic and fully compatible (miscible) plasticizers for the new generation of energetic binders such as polyNIMMO or polyGLYN, in propellant and explosive applications. Crown copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: activated monomer mechanism; α,ω-hydroxy telechelic oligomers; α,ω-nitrato telechelic oligomers)

Introduction

Propellant and explosive compositions have traditionally used a high-energy crystalline compound as the explosive filler in an inert polymeric binder matrix made from the urethane crosslinking of hydroxy-terminated polybutadiene. Recently, hydroxy-terminated polyethers bearing pendent energetic functional groups such as azido and nitrato have become commercially available[1-4] and are deemed to be substitutes for polybutadiene. These materials have been referred to as 'energetic binders' because the presence of the energetic functional groups on the polymer allows the final composition to have a correspondingly reduced amount of the more hazardous high-energy filler to achieve a given performance, yet the composition is less susceptible to external stimuli such as heat. Alternatively, an enhanced performance may be achieved if an energetic binder is used instead of polybutadiene for a given level of filler.

In our laboratories we have prepared nitrato (or nitrate ester) polyethers ranging from low-molecular-weight linear and cyclic oligomers to relatively high-molecular-weight polymers ($M_n \approx 100\,000$). In this paper we report the synthesis and end-nitration of linear energetic oligomers prepared via the activated monomer mechanism[5]. We have already reported the polymerization of oxetane by the activated monomer mechanism (AMM)[6], which we studied as a model compound for 3,3-(nitratomethyl) methyl oxetane (NIMMO) (**I**), and will describe here the similar preparation of polyNIMMO and polyGLYN from glycidyl nitrate (GLYN) (**II**). A more detailed account of the synthesis and properties of higher-molecular-weight polyGLYN appears elsewhere in this journal[7].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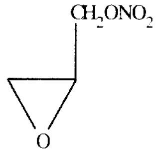
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Experimental

The hydroxy telechelic oligoethers were prepared by the cationic activated monomer method and then end-nitrated.

Reagents. The monomers **I** and **II** were synthesized by the nitration of the respective alcohols and are reported elsewhere[8,9]. Dinitrogen pentoxide was prepared in-house, stored as a white solid at −60°C, and used as a solution in dichloromethane[8]. In all cases, the dichloromethane used was purchased from Romil Chemical Co. and distilled over CaH_2. Tetrafluoroboric acid in diethyl ether, glycerol and 1,4-butanediol (Aldrich Chemical Co) were used as received.

Synthesis of linear α,ω-hydroxy telechelic polyNIMMO of low molecular weight. The synthesis of linear, low-molecular-weight polyNIMMO was carried out using oven (120°C) dried glassware and under an inert, dry

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N_2 atmosphere. NIMMO monomer was vacuum (2–5 mmHg) distilled between 70 and 80°C. The monomer (10 g, 0.068 mol) was made up to a 5% solution in distilled CH_2Cl_2. To a 250 cm^3 jacketed vessel, kept at a temperature of 17°C, 0.39 g (4.328×10^{-3} mol) of 1,4-butanediol was added followed by 0.12 g of 85% tetrafluoroboric acid in diethyl ether (6.30×10^{-4} mol). The ratio of OH : H^+ was 14 : 1. The monomer solution was added over 16 h and the reaction mixture stirred for 4 h. The reaction was quenched with water and neutralized using 5% aqueous $NaHCO_3$. The mixture was separated, the organic layer removed and the CH_2Cl_2 evaporated to leave the polymer. The yield of polyNIMMO was 9.51 g (91.5%, including correction for butanediol incorporation). The polymer was characterized by size exclusion chromatography (s.e.c.), nuclear magnetic resonance spectroscopy (n.m.r.), infra-red spectroscopy (i.r.) and differential scanning calorimetry (d.s.c.).

Synthesis of linear, short chain, end-nitrated polyNIMMO. The synthesis of linear, low-molecular-weight polyNIMMO is described above. The polymer was first dried in a vacuum oven (20°C for 3 weeks). To a sample of linear polyNIMMO (0.476 g, 0.50 mmol) in dichloromethane (11 cm^3) at −21°C was added rapidly a dichloromethane solution of N_2O_5 (6.5 cm^3, 0.18 g, 1.66 mmol); the solution temperature was observed to rise to −13°C before cooling was re-applied, reducing the temperature to −20°C. The solution was allowed to warm to 0°C before the mixture was poured into 10% potassium carbonate solution (aqueous, 100 cm^3) and agitated to ensure thorough mixing. The dichloromethane phase was separated, washed with water (20 cm^3), dried over magnesium sulfate, the dichloromethane removed by vacuum distillation and the sample dried *in vacuo* for approximately 2 h to yield 0.391 g. The polymer was characterized by s.e.c., n.m.r., i.r. and d.s.c.

Synthesis of trifunctional hydroxy-terminated oligomeric glycidyl nitrate. To a 250 cm^3 two-necked flask, jacketed in a water bath (20°C), was added glycerol (5 g, 0.0543 mol) in a four-fold excess of dichloromethane. To this was added HBF_4 (1.7 g, 0.01 mol) and stirring commenced. Glycidyl nitrate (38.77 g, 0.32 mol) was then added over an 18 h period as a 25% solution in dichloromethane. Shortly after HBF_4 addition white fumes were observed, followed by the formation of a pink–purple colour. A further 4 h of stirring were allowed after monomer addition was completed. The mixture was neutralized with aqueous 5% $NaHCO_3$ solution, the organic layer separated and the solvent evaporated to leave a pink viscous liquid. It was also noted that glycerol was not totally soluble in dichloromethane but, as monomer was added, the solution became homogeneous. The final material was analysed by s.e.c., n.m.r. and d.s.c.

End-nitration of trifunctional oligomeric glycidyl nitrate. The trifunctional hydroxy-terminated oligomer (5.49 g) was placed in a 50 cm^3 round-bottomed flask, dissolved in 25 cm^3 dichloromethane and cooled to −20°C. A solution of N_2O_5 (2.6 g, 0.024 mol) in dichloromethane (5% w/v) was slowly added over 5 min. After a further 5 min the reaction was quenched with excess aqueous 10% K_2CO_3 solution. The organic layer was separated and the solvent removed to leave a yellow viscous liquid. This was characterized by s.e.c., n.m.r. and d.s.c.

Instrumentation. Size exclusion chromatography was carried out using four Polymer Laboratories 10 μm columns of 10^5, 10^4, 10^3 and 10^2 Å arranged in series and a Waters system, for glycidyl nitrate compounds, or a Viscotek system for NIMMO compounds. In both cases the refractive index detector traces were used for analysis with the aid of polytetrahydrofuran (polyTHF) standards calibration, with THF as solvent.

A Bruker MSL-300FT n.m.r. spectrometer was used to obtain ^1H spectra at 300.13 MHz and ^{13}C spectra at 75.46 MHz. All samples were recorded at ambient temperature (~22°C) as solutions in $CDCl_3$, with tetramethylsilane as internal reference, at a concentration of about 3% for ^1H and 15% for ^{13}C measurements. For the ^1H spectra, 16 scans were recorded with a delay between pulses of 5.0 s. For broadband decoupled ^{13}C spectra, typically 5000 scans were accumulated, with a delay between pulses of 3.0 s. For semi-quantitative runs, a gated decoupling pulse sequence was used to suppress the nuclear Overhauser enhancement, with a pulse delay of 5.0 s.

A Polymer Laboratories d.s.c., calibrated using indium, sapphire and mercury standards for low-temperature work, was used to study the thermal properties of the compounds and in particular the glass transition temperature (T_g). The glass transition temperature was taken as the mid-point temperature. Heating rate was set at 10°C min^{-1}.

The infra-red spectra were acquired as liquid films between KBr discs on a Nicolet 710 Fourier transform infra-red spectrophotometer at 4 cm^{-1} resolution.

Results and discussion

The synthesis and characterization of the NIMMO compounds are discussed first, followed by the GLYN compounds, and finally the similarities and differences between the two sets of materials are considered.

The molecular weights of the hydroxy-terminated and end-nitrated oligomers of NIMMO were first determined by s.e.c. using the Viscotek system. *Figures 1* and *2* show the traces of the two compounds, which are both similar. This indicates that the use of N_2O_5 as a nitrating agent does not markedly affect the molecular weight distribution, either through crosslinking of chain scission

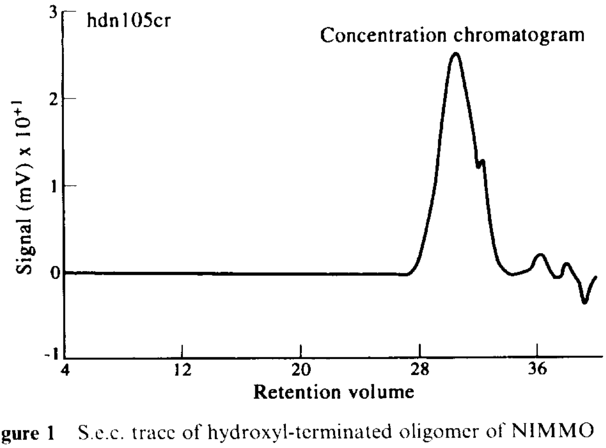


Figure 1 S.e.c. trace of hydroxyl-terminated oligomer of NIMMO

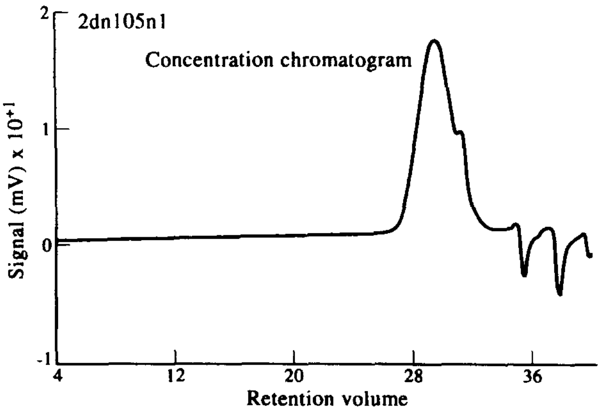


Figure 2 S.e.c. trace of nitrato-terminated oligomer of NIMMO

reactions, unlike other nitrating agents with certain polymers[10]. However, a slight increase in molecular weight should be expected due to the replacement of the hydroxyl proton by the bulkier nitro group.

The Viskotek s.e.c. system using the 'Unical 1' calibration calculates the number-average molecular weight (M_n) of the hydroxyl-terminated oligomer of NIMMO as 450, the weight-average molecular weight (M_w) as 850 and the dispersity (D) as 1.9. The values of the corresponding end-nitrated oligomer for M_n, M_w and D are calculated as 750, 1450 and 1.9, respectively. The dispersities show that the molecular weight distribution has not changed significantly; however, replacement of two protons from the ends of the linear difunctional oligomer by two $-NO_2$ groups should lead to an increase in molecular weight of only 90. Instead, the M_n and M_w values have increased significantly more than 90. Two possible explanations for this can be put forward: (1) the end-nitrated oligomer does not interact as strongly with the size exclusion columns, compared with the hydroxy-terminated oligomer, and is eluted quicker; and (2) it can be seen that all the peaks of the end-nitrated trace, including solvent peaks, have eluted quicker, suggesting that there is a slight instrumental error between the two traces. In order to check this, the samples were re-run immediately one after the other under the same s.e.c. conditions. This was repeated several times and it is found that these NIMMO oligomers, in fact, have nearly identical distributions (*Figure 3*). Re-calculated M_n, M_w and D, using polyTHF standards, for the hydroxyl-terminated oligomer are 1150, 1700 and 1.5 respectively, and for the end-nitrated oligomer are 1150, 1700 and 1.5 respectively. This indicates that there was an instrumental error which shifted the peaks of the end-nitrated sample when it was originally analysed. Nevertheless, as the D values agree, irrespective of the method of analysis, it can be concluded that degradative or chain scission reactions have not occurred upon nitration and that the compounds prepared are oligomers. The effect of end-nitration on hydrodynamic volume is discussed further, below, in conjunction with the s.e.c. analysis of the GLYN oligomers.

The oligomeric nature is confirmed by the ^{13}C n.m.r.

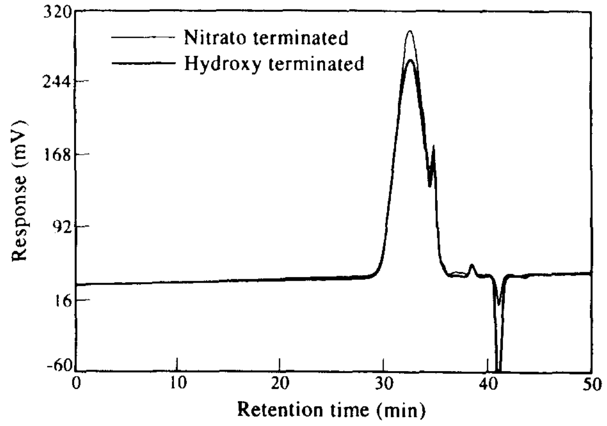


Figure 3 Typical repeated s.e.c. traces of NIMMO oligomers

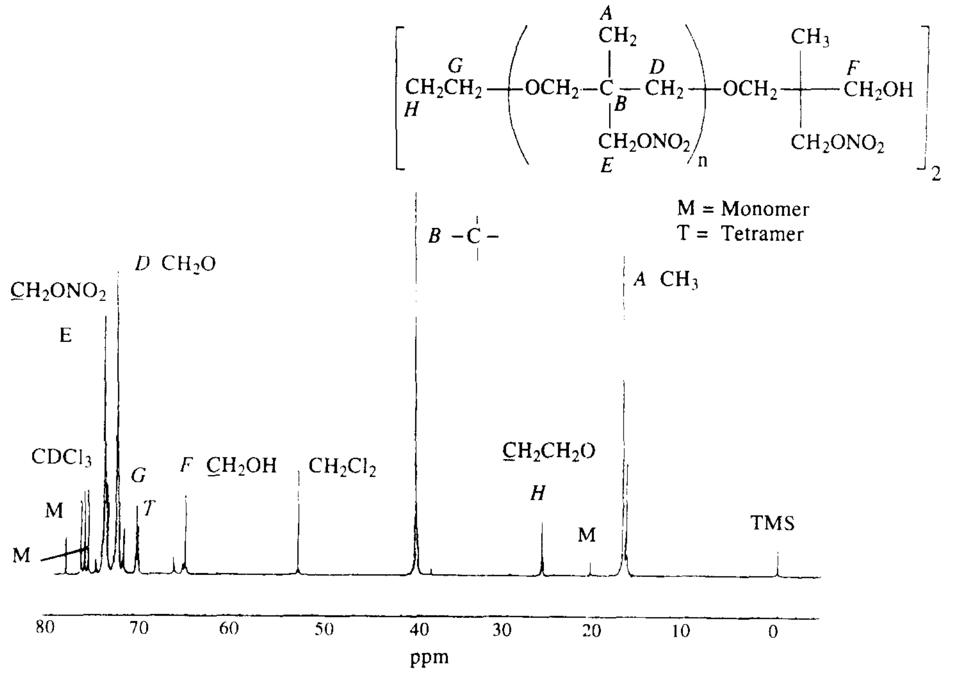


Figure 4 ^{13}C n.m.r. spectrum for hydroxyl-terminated NIMMO oligomer

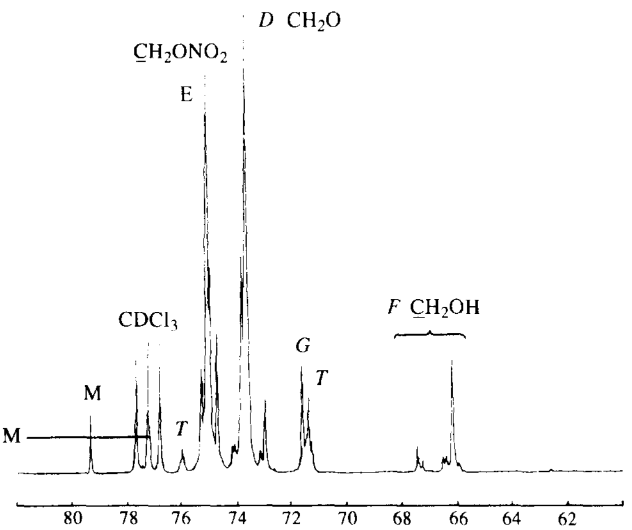


Figure 5 Expanded ^{13}C n.m.r. spectrum for hydroxyl-terminated NIMMO oligomer

spectra of the hydroxy-terminated compound (*Figures 4* and *5*) which show the CH_2OH end-groups (peaks F in the structure), the in-chain NIMMO $-OCH_2$ (peaks D) and the $-CH_2ONO_2$ peaks (E). From the integral of the $-CH_2OH$ peaks and the in-chain peaks D and E, the value of n in the structure (*Figure 4*) is calculated to be 2.7, which gives a value of M_n of about 1180. This should be a reasonably reliable estimate of the molecular weight of the oligomers, and corresponds to about 7.4 NIMMO units including the two end ones. It is noteworthy that polyTHF equivalent molecular weights agree with n.m.r. values but 'Unical' values are lower. The reasons for this anomaly are not clear and henceforth only polyTHF equivalent molecular weights are quoted.

The ^{13}C n.m.r. spectra of the NIMMO oligomers also confirm the proposed structures. As indicated on the spectra, all the major peaks can be readily assigned. The almost complete absence of peaks at about 30 and 63 ppm (*Figure 4*), which would be due to 1,4-butanediol end groups, is noteworthy, as polyNIMMO samples prepared by the active chain-end mechanism often show butanediol end-groups. The central $-CH_2$ peaks of the 1,4-butanediol units ($-OCH_2\underline{C}H_2\underline{C}H_2CH_2O-$) appear almost exclusively at about 26 ppm, indicating that they are incorporated into the 'middle' of the chains as $-CH_2OCH_2CH_2CH_2CH_2OCH_2-$ units rather than as $-CH_2CH_2CH_2CH_2OH$ end-groups. This is characteristic of an activated monomer polymerization. The samples also show the presence of dichloromethane, monomer and cyclic tetramer.

The corresponding spectra of the end-nitrated oligomer of NIMMO (*Figures 6* and *7*) are very similar to *Figures 4* and *5*, as expected. The main difference is that the peaks between 66 and 68 ppm in *Figures 4* and *5*, which were assigned to the $-CH_2OH$ end-groups, have disappeared, indicating their efficient nitration. The end hydroxyl groups are converted to $-CH_2ONO_2$ groups and therefore become similar to in-chain $-CH_2ONO_2$ groups in band E. The fact that bands E and D show several peaks with slightly different chemical shifts, whereas higher molecular weight polyNIMMO shows only one peak for each, is due to the oligomeric nature of the samples.

The infra-red spectrum of the end-nitrated NIMMO oligomer (*Figure 9*) shows that both the OH bands (3619, 3439 cm^{-1}), which are present in the hydroxy-terminated oligomer (*Figure 8*), have disappeared. This suggests that terminal hydroxy groups have reacted with N_2O_5 to form nitrato end-groups.

From the analysis of these compounds the reactions of synthesis are shown in *Scheme 1*.

As the materials are envisaged as plasticizers, their thermal properties were studied by d.s.c. The clear, pale yellow liquids show an endothermic transition, glass transition, which is the dominant feature. The hydroxy-

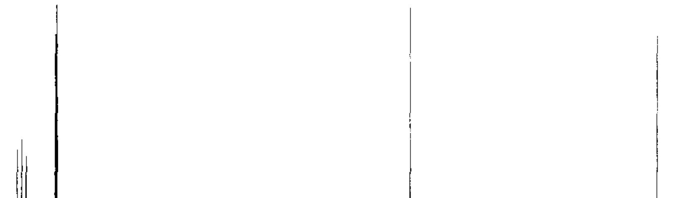


Figure 6 ^{13}C n.m.r. spectrum of nitrato-terminated NIMMO oligomer

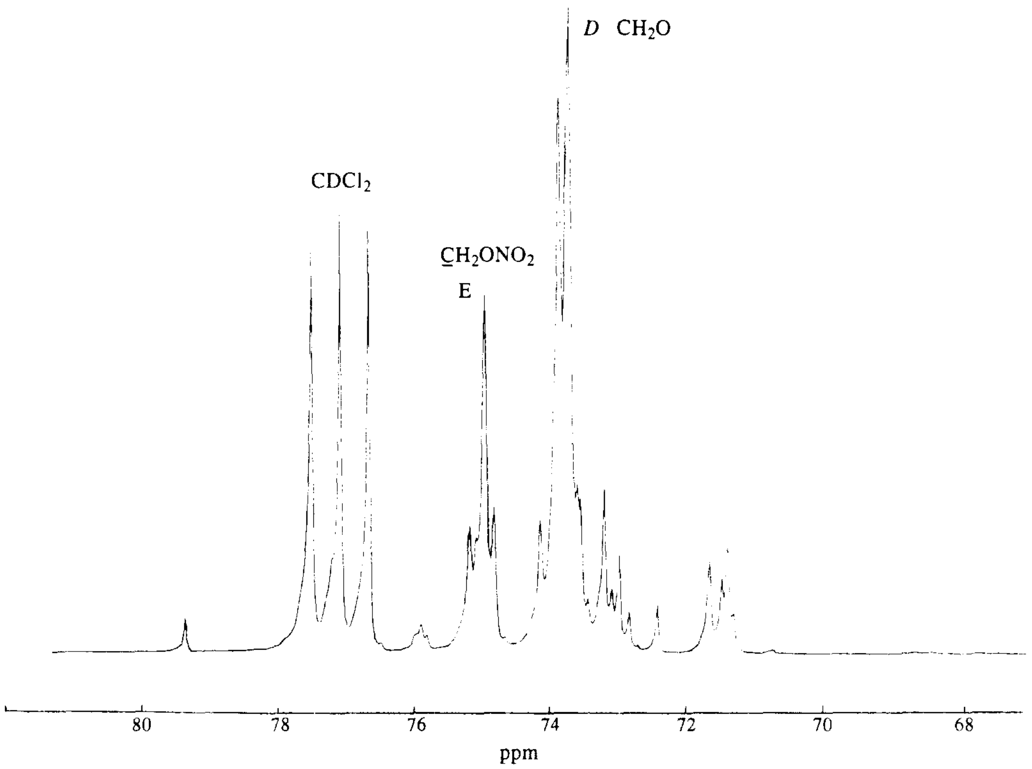


Figure 7 Expanded ^{13}C n.m.r. spectrum of nitrato-terminated NIMMO oligomer

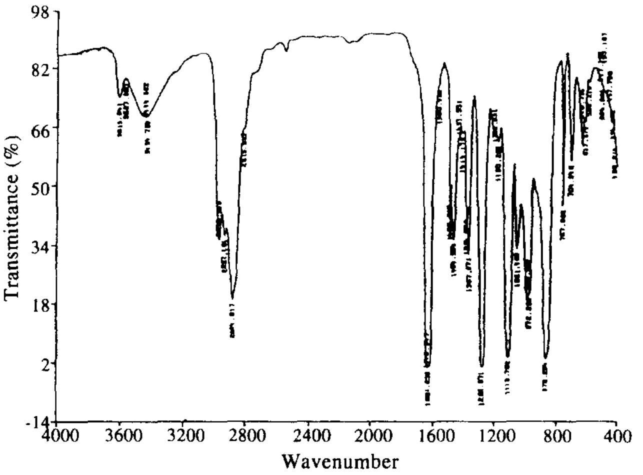


Figure 8 *FT*i.r. spectrum of hydroxy telechelic oligomer of NIMMO

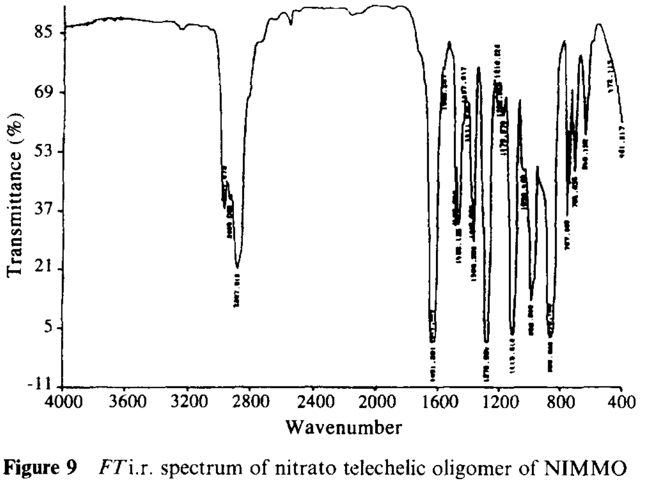


Figure 9 *FT*i.r. spectrum of nitrato telechelic oligomer of NIMMO

terminated oligomer shows a transition at −33°C while the end-nitrated oligomer shows a transition at −39°C. The lower transition of the end-nitrated oligomer may be due to the reduction in hydrogen bonding interactions between the hydroxy groups upon nitration. It should also be noted that the glass transition temperature (T_g) of a polymer rises with increasing molecular weight[11] and, indeed, the T_g of linear difunctional polyNIMMO[12] of molecular weight 4000 usually has a transition at about −25°C. Another feature, probably leading to a lower T_g for these compounds compared with the 4000 molecular weight polyNIMMO, is the presence of small amounts of cyclic species, which may also be acting as plasticizers.

The methods of synthesis and the results of analyses of the glycidyl nitrate oligomers are similar to NIMMO oligomers. The main differences are that the trifunctional or three-armed oligomer of GLYN is prepared and that cyclic impurities are not detected. *Figure 10* compares the s.e.c. traces of hydroxy-terminated and N_2O_5-reacted

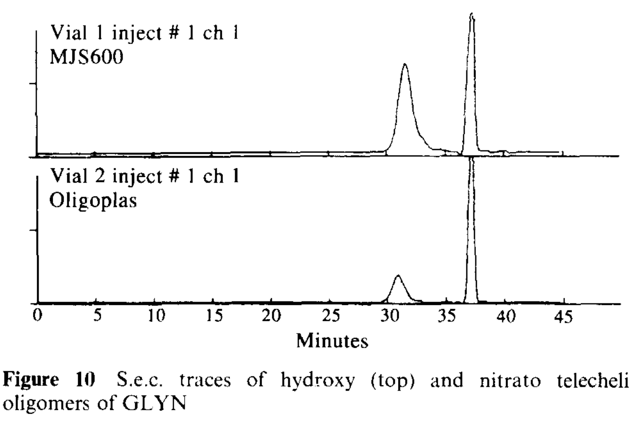
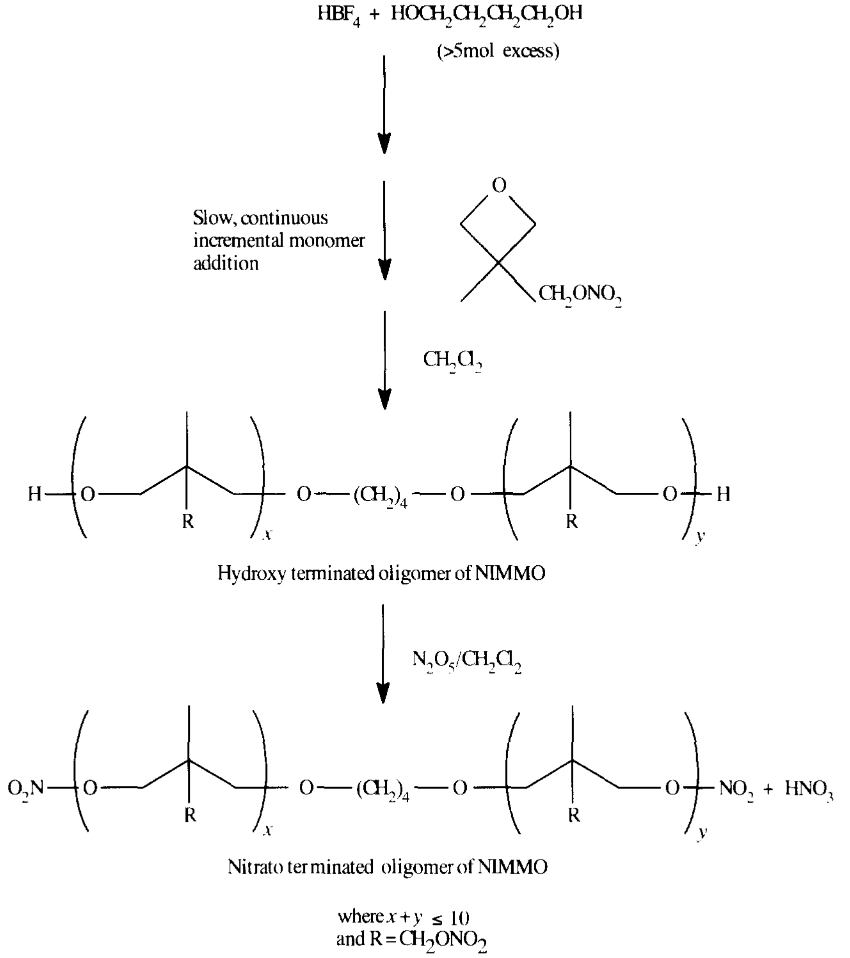


Figure 10 S.e.c. traces of hydroxy (top) and nitrato telechelic oligomers of GLYN



Scheme 1 The activated monomer synthesis of hydroxy-terminated oligomer of NIMMO followed by end-nitration to form the nitrato-terminated oligomer

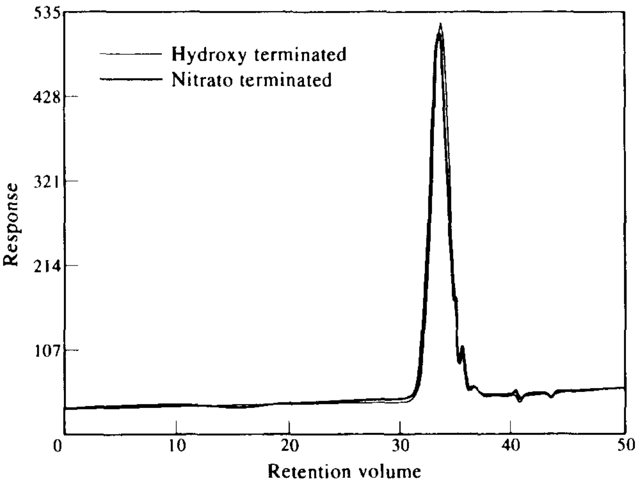


Figure 11 S.e.c. traces of repeated syntheses of GLYN oligomers

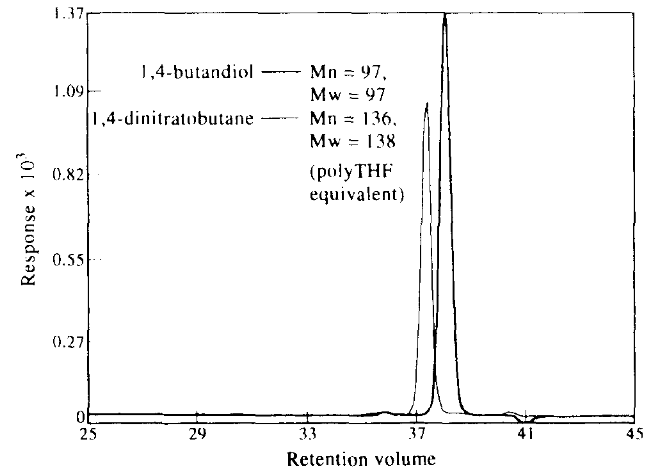


Figure 12 Expanded s.e.c. traces of 1,4-butanediol and 1,4-dinitratobutane

oligomers of GLYN. Unlike the NIMMO oligomers, the nitrated GLYN compound shows a discernible shift of the main peak to lower elution volume. To ensure that this was not due to s.e.c. instrumental error, the synthesis of the GLYN oligomers was repeated and the samples re-run several times in 'pairs', i.e. the hydroxy oligomer was run just before the nitrated oligomer so that instrumental variation was minimized. *Figure 11* shows that there is indeed a slight shift of the end-nitrated peaks to lower elution volumes and the M_n, M_w and D values (polyTHF equivalent) change from 700, 900 and 1.3 for the hydroxy-terminated oligomer to 750, 900 and 1.2, respectively, for the nitrato-terminated oligomer. The similar dispersities of the compounds suggests that degradative reactions do not occur. However, the calculated M_n of the nitrated oligomer does not increase as much as expected compared with the hydroxy compound, and this may be due to the inadequate resolving power of the s.e.c. system used or the effect of branching on hydrodynamic volume. The observation that the GLYN samples show a discernible shift of the nitrated compounds to lower elution volumes whereas the nitrated and hydroxy-terminated NIMMO oligomers overlap may be because of the lower molecular weight and branching of the GLYN oligomers. End-group modification should have a greater effect on hydrodynamic volume if a sample is of lower molecular weight. To investigate this and to examine the sensitivity of the s.e.c. system used, 1,4-butanediol and 1,4-dinitrato butane were analysed (*Figure 12*) and this indicates that nitration does affect hydrodynamic volume. Further work needs to be carried out to determine the magnitude of the effect of end-nitration on hydrodynamic volume and its dependence on molecular weight and/or branching.

The n.m.r. spectra of the GLYN compounds are more complicated than those of the NIMMO species. *Figure 13* shows the ^{13}C n.m.r. spectrum, in acetone-D_6, of a typical GLYN oligomer sample prepared by the activated monomer method, using glycerol as the alcohol. It is observed that $-OCH_2$ peaks occur at about 70 ppm, $-CH_2ONO_2$ peaks at about 74 ppm and $-OCH$ peaks at about 77 ppm. The spectrum also shows the presence of monomer and methylene chloride. The ^1H n.m.r. spectrum of hydroxy-terminated GLYN oligomer, *Figure 14*,

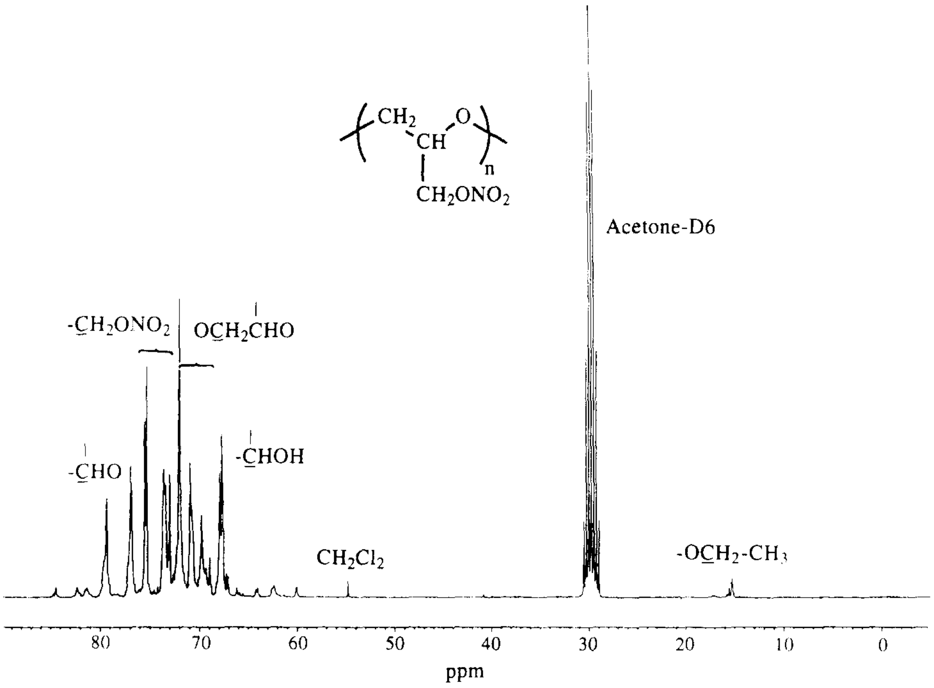


Figure 13 ^{13}C n.m.r. spectrum of hydroxyl-terminated GLYN oligomer

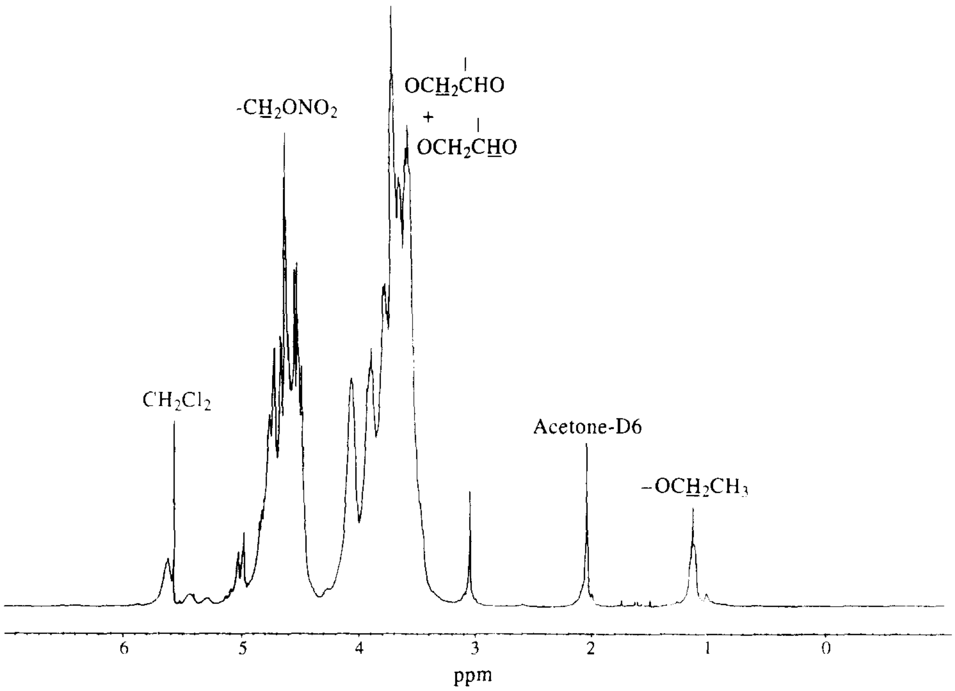


Figure 14 ^1H n.m.r. spectrum of hydroxyl-terminated GLYN oligomer

is consistent with the proposed structure of a nitrated polyoxirane.

Figures 15 and *16* show the ^{13}C and ^{1}H n.m.r. spectra, respectively, of the end-nitrated GLYN oligomer in acetone-D_6. This material is based on glycerol as initiator and therefore does not show the characteristic 1,4-butanediol peaks usually observed when 1,4-butanediol is the initiator. The overall spectra are consistent with the proposed oligomers, although it has not yet been possible to make such a detailed assignment as for the NIMMO case. The ^{13}C n.m.r. spectrum does show peaks at about 70, 74 and 78 ppm, probably corresponding to $-OCH_2-$, $-CH_2ONO_2$ and $-OCH-$, respectively.

The greater complexity of the GLYN samples, compared with NIMMO oligomers, is consistent with their proposed structure. Firstly, as the materials are thought to be trifunctional and of low molecular weight, about 700, then each chain would have on average six GLYN units. This would correspond to only two units per branch, and therefore none of these would be in the same environment as an in-chain unit from a higher molecular weight polymer. Secondly, we expect a given

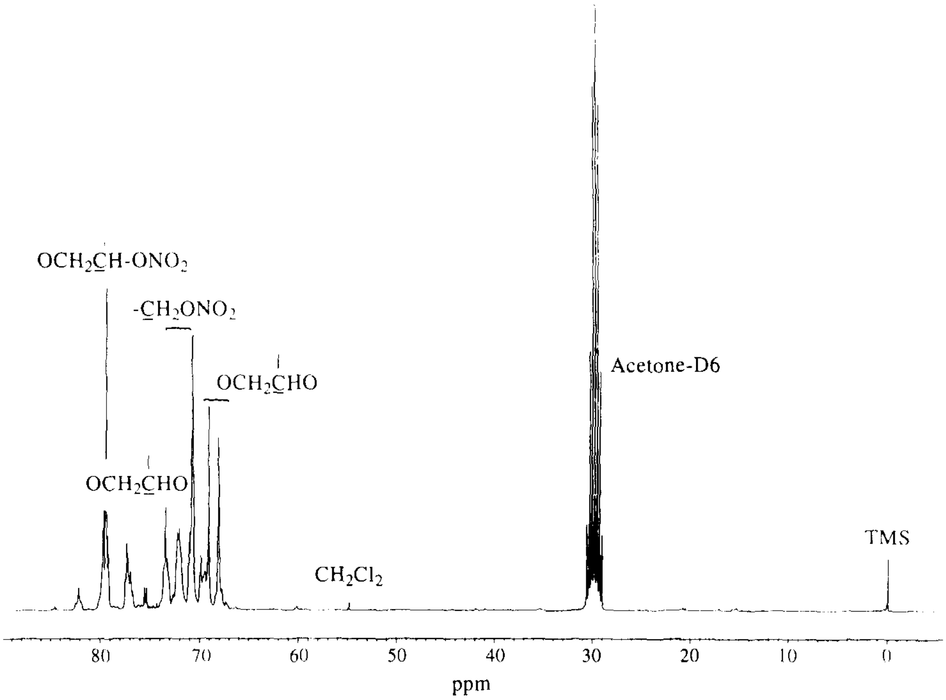


Figure 15 ^{13}C n.m.r. spectrum of end-nitrated GLYN oligomer

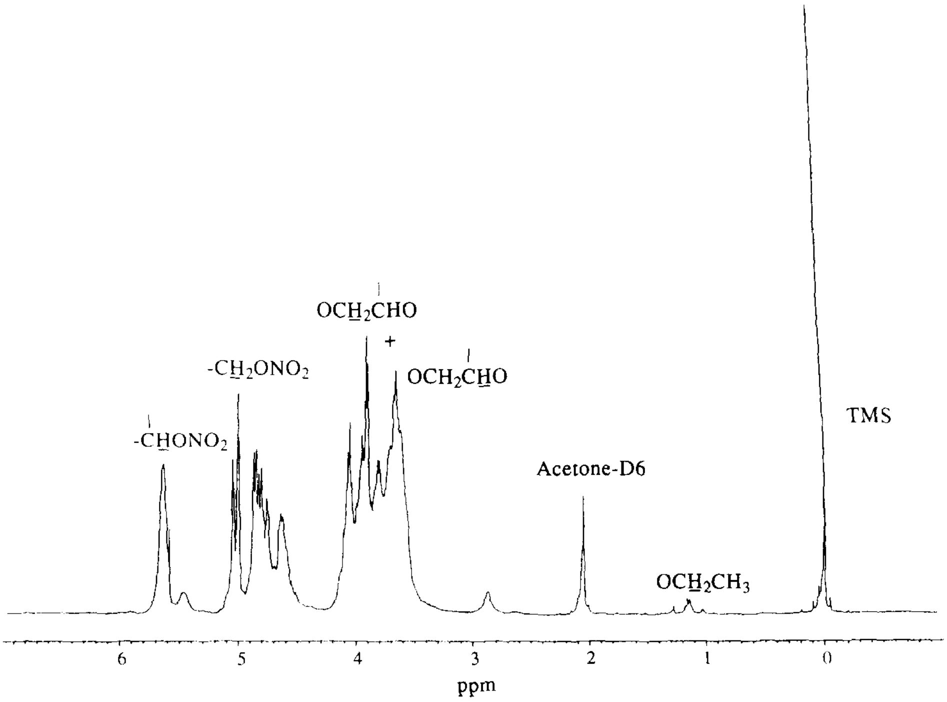
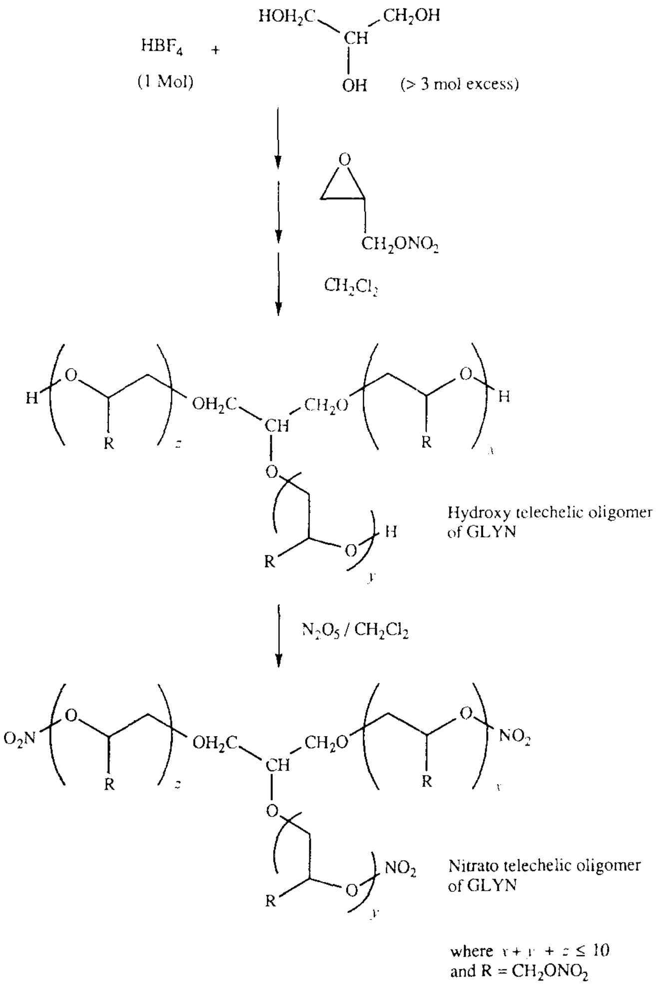


Figure 16 ^{1}H n.m.r. spectrum of end-nitrated GLYN oligomer



Scheme 2 Synthesis of the hydroxy and nitratotelechelic oligomers of GLYN

GLYN unit in a GLYN polymer or oligomer to be more influenced by its neighbour than an analogous NIMMO unit, reflecting the polyoxirane rather than polyoxetane structure.

Differential scanning calorimeter traces of GLYN oligomers confirm the phenomenon observed for NIMMO oligomers in that the nitrated oligomer has a lower T_g, −32°C, compared with the hydroxyl-terminated oligomer, −26°C. The magnitude of the change is again 6°C but this is probably a coincidence. Nevertheless, it is apparent that nitration affects the thermal behaviour of the oligomers. The mode of synthesis is similar to that of preparing NIMMO oligomers and is shown in *Scheme 2*.

Conclusion

Novel hydroxy and nitrato telechelic oligomers of monomers bearing negatively inductive substituents, namely 3,3-(nitratomethyl) methyl oxetane and glycidyl nitrate, have been prepared by careful control of cationic polymerization systems. The activated monomer mechanism has been used to form the hydroxy oligomers, which have then been modified using dinitrogen pentoxide to form nitrato oligomers, without side reactions, e.g. chain scission. The nitrato oligomers have a lower T_g than the corresponding hydroxy compounds. The materials are expected to act as energetic and fully compatible plasticizers in new propellant and explosive formulations.

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