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Synthesis of narrow molecular weight α,ω-hydroxy telechelic poly(glycidyl nitrate) and estimation of theoretical heat of explosion

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This communication reports the synthetic steps and characterization required to make pure poly(glycidyl nitrate), also known as polyGLYN or POWA3, from cheap commercially available starting materials using dinitrogen pentoxide (N_2O_5) technology. Conditions are given whereby a range of well defined and characterized polyGLYN samples may be safely and reproducibly prepared by the cationic, ring-opening, activated monomer mechanism (AMM). Tetrafluoroboric acid and 1,4-butanediol were used as the catalyst system, and the samples have been characterized by nuclear magnetic resonance spectroscopy, size exclusion chromatography, infra-red spectroscopy and differential scanning calorimetry. The theoretical calculations indicate that the heat of explosion is 2661 kJ kg^{-1}, this being significantly more energy than for earlier polymers. These materials are currently under assessment in both high-performance explosives and high-energy low-vulnerability propellant systems. Some properties of the material are also shown. Crown copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: dinitrogen pentoxide; poly(glycidyl nitrate); activated monomer mechanism)

Introduction

Over the last few years considerable effort has been devoted to the synthesis and characterization of intrinsically energetic polymers for use as binders in propellant and explosive compositions. An energetic polymer may be defined as a macromolecule bearing functional groups rich in chemical energy, e.g. nitro, azido or, as in this case, nitrato moieties. To date, three main classes of energetic binder have been shown to possess the necessary combination of acceptable properties and facile synthesis which make them candidates for widespread use within the explosives and propellant community. These are nitrated hydroxy-terminated polybutadiene[1], an energetic azido-oxirane binder known as glycidyl azide polymer (GAP)[2] and poly(3,3-nitratomethyl methyl oxetane), also referred to as polyNIMMO, polyNMMO or POWAI[3,4]. Unfortunately, most other materials have been exotic in nature and consequently are ill-suited to commercial manufacture. Subject to the materials possessing acceptable properties, scope therefore still exists for the development of cost-effective routes to energetic binders.

In this paper we describe the relatively convenient, scaleable and, above all, safer synthesis of an energetic polyether based on the ring-opening of a nitrato-substituted oxirane monomer, known as glycidyl nitrate or GLYN (**I**). Poly(glycidyl nitrate) (polyGLYN) was first prepared[5–7] in the 1950s but the batchwise synthesis of the monomer and its subsequent purification, along with the 'all monomer in' polymerization, were considered to be too hazardous. This was due to poor control over exotherms associated with the nitration and polymerization steps which, it was feared, may lead to an explosive decomposition of the energetic nitrato group.

This communication describes the safer synthesis and the theoretical heat of explosion of α,ω-hydroxy telechelic poly(glycidyl nitrate), which may be cured into an energetic binder.

Experimental

Materials. Glycidol (Aldrich or BDH) was supplied as 96% pure with oligomer contamination. This was redistilled on a rotary evaporator at 50°C to remove high-molecular-weight species and stored at −10°C until use. Dinitrogen pentoxide (N_2O_5) free from nitric acid and lower oxides was prepared by ozonation[8] of N_2O_4. Colourless (white) crystals of N_2O_5 were stored at −78°C. Unstabilized, analytical grade dichloromethane (Romil Chemicals) was dried over CaH_2, then fractionally distilled under nitrogen. 1-Butanol, 1,4-butanediol and glycerol were purchased from Aldrich Chemical Co. as >99% pure and used under nitrogen as supplied. Tetrafluoroboric acid etherate (Aldrich) was also stored under nitrogen, refrigerated and used as supplied.

Equipment. Although activated monomer polymerizations are far more tolerant of water than cationic oxonium polymerizations, the presence of protonic species can adversely affect the molecular weight. Care was therefore taken to ensure that all polymerization

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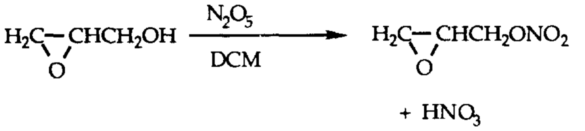
reactors, syringes and needles were clean, dry and free from visible contaminants. Excessive cleaning precautions such as those required in ionic, particularly anionic, polymerizations were not considered necessary.

Flow nitration preparation of glycidyl nitrate. Safety note: owing to the extremely sensitive product formed during the nitration reaction, this procedure should be carried out in an armoured cupboard with fume extraction.

The reaction equation for the nitration is as follows:



(I)

However, this is not the only reaction possible and side reactions leading to the formation of nitroglycerine as well as glycerol dinitrate also occur. Moreover, there is an exotherm associated with all these reactions.

To overcome the problems of an exotherm and side reactions, a flow reactor technique was adopted. This technique was adapted to produce a dichloromethane (DCM) solution of GLYN in very high yield (>95%) and of such a high purity (>99%) that no further purification was required prior to polymerization. Suppression of the secondary reactions was achieved by control of the residence time in the flow reactor and of the reaction exotherm. The reaction time is of the order of seconds and the reactor output is immediately quenched with an aqueous carbonate wash to remove both the nitric acid and the small excess of N_2O_5 which is necessary to ensure complete reaction. A detailed account of this technique may be found in ref. 9.

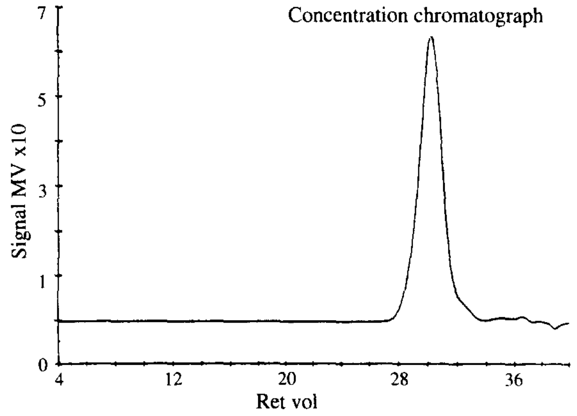


Figure 1 Size exclusion chromatograph of a polyGLYN sample free of oligomer and monomer contamination. 'Universal Calibration' equivalent molecular weights (as opposed to THF equivalent) for the sample shown above are: $M_n = 1300$; $M_w = 2000$; $D = 1.5$; $M_p = 1750$

Preparation of poly(glycidyl nitrate). Safety note: owing to the acute hazards associated with the neat monomer, and to a lesser extent the polymerization, this reaction should also be carried out in an armoured cupboard with fume extraction.

The polymerization reactor, which consisted of a 2 l jacketed vessel equipped with flange top, mechanical stirrer, thermometer, nitrogen inlet/outlet and serum cap, was cooled from 120°C to ambient under a stream of nitrogen. The reactor was then connected to a cooling circulator (Haake), and charged with a 25% w/v mixture of 1,4-butanediol in dichloromethane (6.06 g in 25 ml, 0.067 mol). The reactor was cooled under nitrogen to 0°C and a catalytic amount of tetrafluoroboric acid etherate (1.09 g, 6.72×10^{-3} mol) was added. Immediately afterwards a 25% w/v GLYN solution in dichloromethane (400 g, 3.36 mol) was pumped in at a constant flow rate over a period of 40 h. When the addition was complete a further polymerization time of 2 h was allowed before the

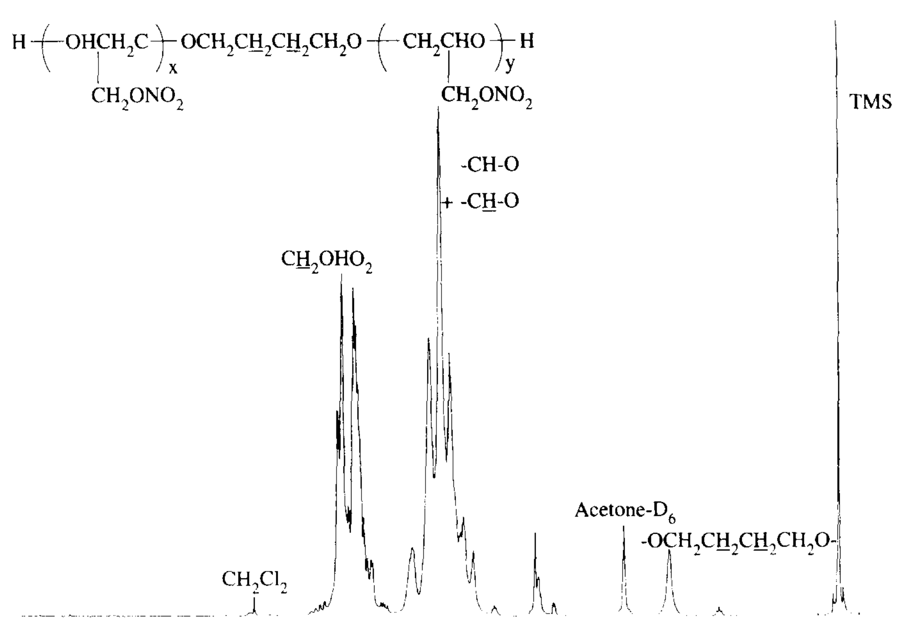


Figure 2 ^1H n.m.r. spectrum of polyGLYN

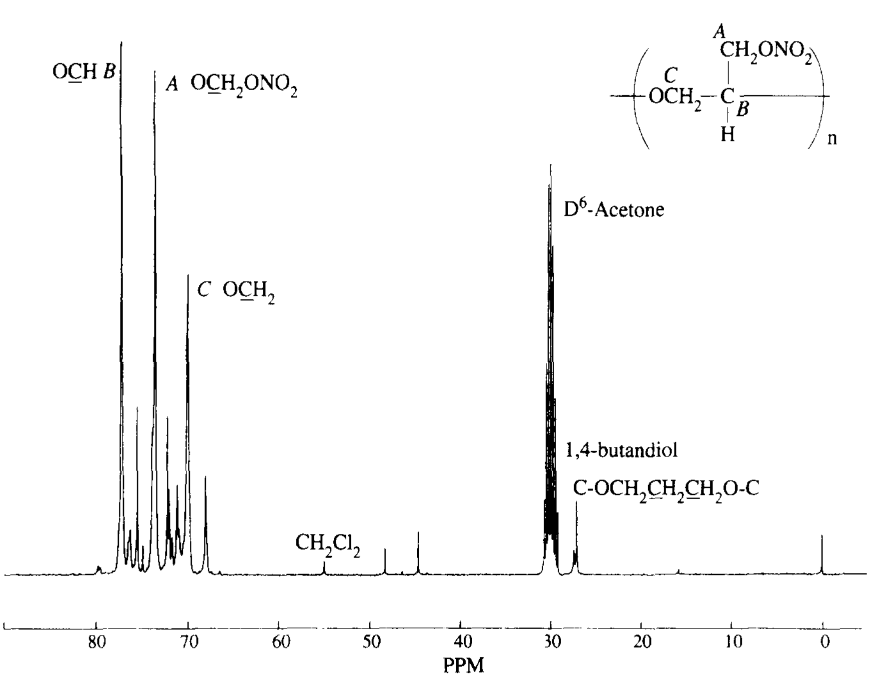


Figure 3 ^{13}C n.m.r. spectrum of polyGLYN

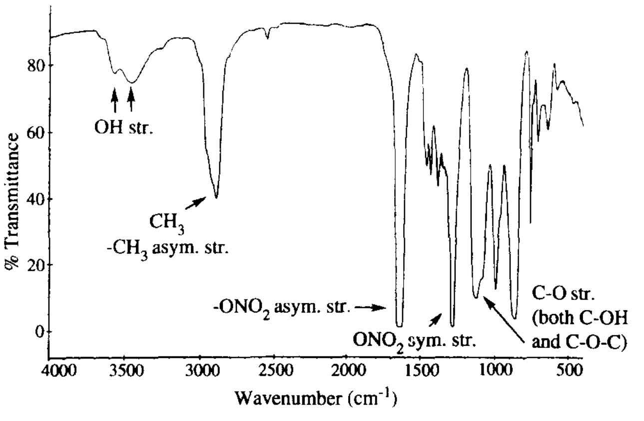


Figure 4 *FT*i.r. spectrum of polyGLYN

reaction was terminated by the addition of a five-fold excess of aqueous sodium hydrogen carbonate (2.52 g, 0.03 mol). Stirring was continued until no further gas evolution was noted, whereupon the lower organic layer was separated from the upper aqueous phase, dried over $CaCl_2$ for 16 h, reduced in volume to about 0.8 l, and fractionally precipitated into excess methanol/water (75/25). The white tacky polymer was isolated, redissolved in dichloromethane (approx. 1 l) dried over calcium chloride and evaporated to dryness. The resultant viscous pale yellow polymer was then dried in a vacuum oven at 60°C for 72 h before use. Yield 308 g (77%). The polymer was characterized by nuclear magnetic resonance spectroscopy (n.m.r.), infra-red spectroscopy (i.r.), differential scanning calorimetry (d.s.c.) and size exclusion chromatography (s.e.c.). The latter employed a Viscotek System with four Polymer Laboratories 10 μm columns of 10^5, 10^4, 10^3 and 10^2 Å arranged in series.

Table 1 Summary of some properties of poly(glycidyl nitrate)

Molecular weight (s.e.c.)	$M_w = 4400$; $M_n = 3000$; $M_w/M_n = 1.46$
Purity (s.e.c., n.m.r.)	>98%
Density (pyknometer)	1.39 g cm^{-3}
Viscosity (Ubbehlode viscometer)	46 Poise at 50°C 163 Poise at 30°C
Glass transition temperature (d.s.c.)	−35°C
Functionality	≤ 2
Miscibility	Miscible with energetic plasticizers, e.g. Metriol trinitrate

Results and discussion

Poly(glycidyl nitrate), which is also known as POWA3, was analysed by s.e.c. (*Figure 1*), to determine its molecular weight distribution, and by n.m.r. (*Figures 2* and *3*) and i.r. (*Figure 4*) spectroscopies, to ascertain its chemical structure. *Table 1* shows some of the physical

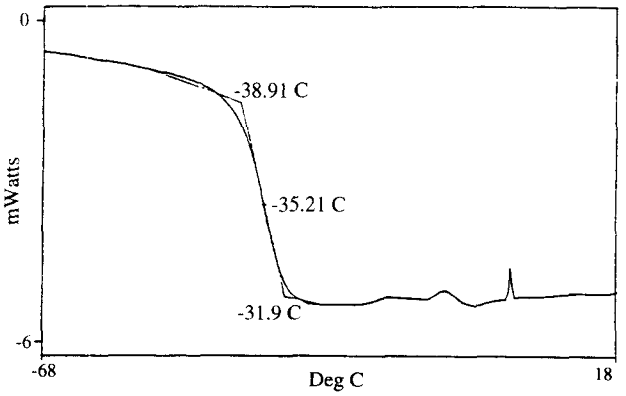


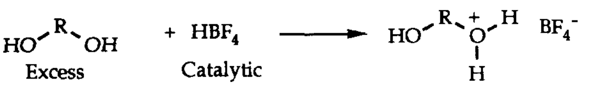
Figure 5 Differential scanning calorimeter trace of polyGLYN showing the glass transition (T_g) at −35°C. The heating ramp rate was set at 10°C per minute and data points were collected between the temperatures of −120°C and +110°C

and chemical properties of polyGLYN, of particular interest are the d.s.c. results (*Figure 5*) indicating the thermal behaviour of the polymer. To begin with, we discuss the chemical structure of the polymer and its relationship with the preparation conditions, which are very closely tied to the mechanism of polymerization. This is followed by relating the properties of the polymer to the structure, so assessing its desirability as a propellant or polymer-bonded explosive (PBX) ingredient. Finally, the theoretical performance of polyGLYN is estimated.

Polymerization. Glycidyl nitrate is polymerized by a cationic technique where the conditions are carefully controlled so that the mechanism of propagation is altered from the conventional 'active chain-end' (ACE), used for cyclic ethers, to an 'activated monomer'[10]. The result of this is a hydroxytelechelic polymer with a narrow molecular weight distribution, i.e. the crude product is almost oligomer and monomer (see *Figure 1*). This is a clear advantage insofar as there is little unreacted monomer in the final propellant or explosive composition which may cause an increase in sensitivity. Hence, using this method, the small amount of monomer (<4%) is easier to remove and in some cases the monomer level may be low enough so that a purification step is not required.

The s.e.c. trace shows a polymer of number-average molecular weight (M_n) of 1300, a weight-average molecular weight (M_w) of 2000 and dispersity of 1.5. Number-average molecular weights of up to 3500 have been achieved. These values are Viscotek's 'universal calibration' equivalents. The dispersity, although close to figures observed for 'living' polymerization systems, which typically have values less than 1.1 but greater than 1.0, indicates that this is not an example of a living-chain growth system. However, adjustment of the monomer-to-alcohol ratio allows the control of molecular weight to synthesize linear hydroxy telechelic oligomers which can be end-nitrated, and as reported elsewhere[11].

The n.m.r. spectra, *Figures 2* and *3*, show that the butanediol fragment is in the centre of a polyGLYN chain and that the terminal hydroxyl groups are due to the ring-opening of the monomer. The mechanism by which the polymerization of glycidyl nitrate proceeds is believed to be as follows: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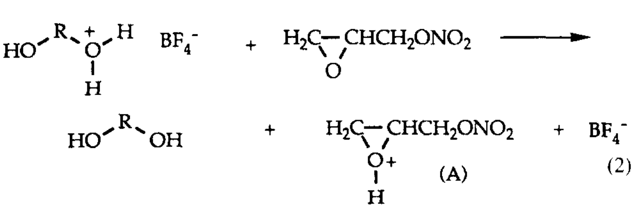
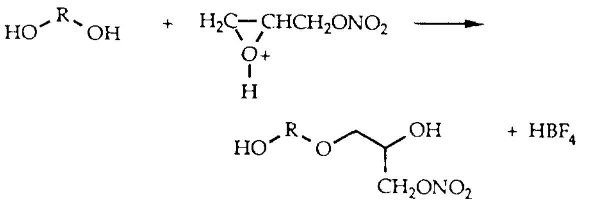

(2)

Activated monomer

This type of polymerization is known as the activated monomer mechanism (AMM) and takes its names from the protonated monomer, species A, which is regenerated after each successive propagation step. In the conventional ACE-type mechanism, species A is also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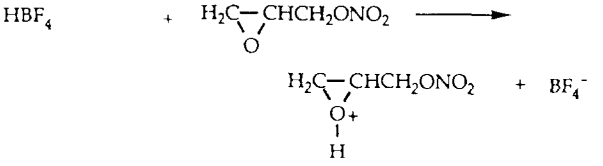
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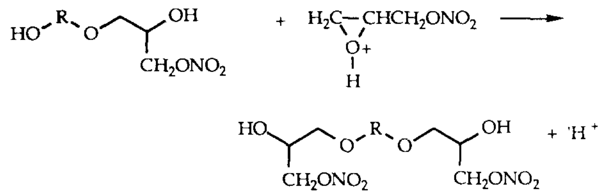
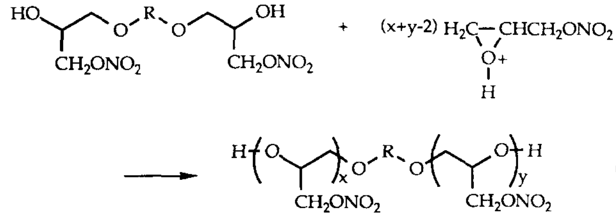
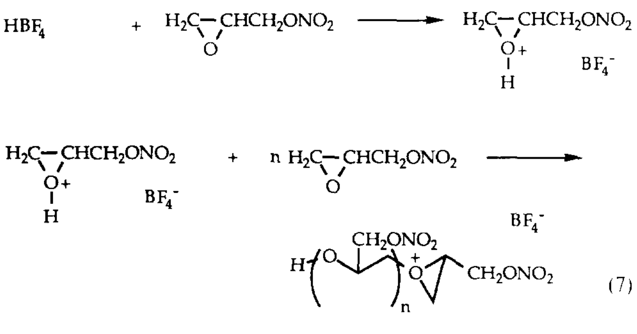

(5)


(6)

polyGLYN

generated but the conditions are such that it reacts with further monomer[12]:


(7)

Active chain-end (C)

Under ACE conditions species C can undergo internal back-biting or end-biting reactions to produce cyclic species, react with impurities causing termination and/or react with counter-ions also causing termination or dormancy. In the case of glycidyl nitrate, ACE experiments produced a very low yield of polymer probably due to the aforementioned termination reactions. In addition to this, as it is well known that neat oxiranes polymerize explosively and that it is difficult to control molecular weight distributions by ACE polymerization, this mode of propagation was considered unsuitable for GLYN. Hence, the AMM was developed to polymerize

GLYN because it enables control of the exotherm and molecular weight (≤ 3500) to produce an α,ω-hydroxytelechelic polymer, free of oligomer contamination. The two key factors in achieving this are the maintenance of at least a tenfold excess of hydroxyl groups over the protonic acid catalyst, tetrafluoroboric acid, and the slow addition of monomer solution between 16 and 40 h.

The former factor ensures that the protonated monomer reacts with the excess of hydroxyl groups. If the ratio of $OH:H^+$ is near to 1 : 1 then the probability of the protonated monomer reacting, within a given time interval, with the hydroxyl group is reduced. Consequently, the protonated monomer level builds up to the extent that further incoming monomer reacts with species A by a predominantly ACE mechanism. The latter factor further suppresses ACE-type propagation because the monomer is fed in at such a rate that the activated monomer cannot react with unprotonated monomer. In other words, the rate of monomer addition has to be less than the rate of monomer protonation and subsequent reaction with a hydroxyl group.

The result of this is the formation of linear polyGLYN chains with hydroxyl end-groups. However, there are disadvantages, partly due to both the nature of the monomer and to limitations of the AMM. First, predominantly secondary hydroxyl groups are formed as electrophilic attack by the oxygen atom (of the hydroxyl group of an existing chain) occurs on the least hindered carbon of the monomer. Second, molecular weights greater than 3500 (M_n) are very difficult to achieve. The reasons for this are probably due to impurities in the monomer feed, alcohol, catalyst and the presence of adventitious moisture in the apparatus. Third, the recovered yield of polymer is around 80%. Clearly, a certain amount of material is lost in the work-up, especially through dissolution of low-molecular-weight alcohols in water. In addition, conversion from monomer to polymer/oligomer is $\sim 95\%$ which necessitates the precipitation stage to reduce monomer levels to acceptable quantities for formulations. Work is under progress to improve conversion as well as to reduce unreacted monomer levels so that a precipitation step is not necessary. This should lead to a significant saving in costs and a reduction in the overall price of the binder. Despite these difficulties concerning the AMM, an energetic polymer with variable functionality, molecular weight and, therefore, viscosity suitable for formulations, is preparable.

Physical and chemical properties relevant to propellant and explosive applications. *Table 1* contains a list of the properties of polyGLYN. The most important of these properties is the glass transition temperature (T_g). The T_g of -35°C (see d.s.c. trace, *Figure 5*) is 10°C lower than that of the less energetic binder, poly(3,3-nitratomethyl methyl oxetane). This makes polyGLYN attractive because the target T_g for service use is -50°C. With the aid of suitable plasticizers, perhaps those made from oligomers of polyGLYN (work is in progress to synthesize, characterize and test the viability of these as plasticizers, and will be the subject of a future report), it should be possible to approach this target T_g and consequently the ultimate goal of insensitive formulations, even at sub-ambient temperatures. Further work is also necessary to study the effect of star architecture or branching[11] and molecular weight on glass transition temperature.

Another property, the enthalpy of explosion (Q_x) is difficult to determine experimentally but a theoretically calculated value based on the following treatment indicates the energy of the compound. Quite a detailed account[13] is given here so that the definitions, assumptions and errors that lead to the final figures may be appreciated.

The enthalpy or heat of explosion is the formation of the explosion products from the solid compound. This is distinct from the heat of combustion (Q_c°), which is the heat of formation of the products of combustion from the solid compound. The data from heats of combustion (experimental) can be used to calculate heats of formation of the various products and these are available. Hence, for an energetic substance with a formula $C_aH_bN_dO_g$

$$Q_x = \sum Q_f^{st}(x) = Q_f^\circ \qquad (8)$$

where $\Sigma Q_f^{st}(x)$ is the sum of the heats of formation of the various explosion products from the elements in their standard states and Q_f° is the heat of formation of the compound from its constituent elements in their standard states.

Similarly, for the heat of combustion

$$Q_c = \sum Q_f^\circ(c) - Q_f^\circ \qquad (9)$$

where $\Sigma Q_f^\circ(c)$ is the sum of the heats of formation of combustion products from the constituent elements in their standard states.

If combustion data are not available then Q_f° can be calculated by the relation

$$Q_f^\circ = Q_f^a(g) - \Sigma Q_{st}^a(E) - L_v - L_f \qquad (10)$$

where $Q_f^a(g)$ is the heat of formation of the compound, in the gas-phase, from the free ground-state atoms of its constituent elements. $\Sigma Q_{st}^a(E)$ is the sum of the heats of formation of the individual constituent elements in their standard states (C as graphite) from the free atoms in their ground-states. L_v and L_f are the latent heats of fusion and vaporization, respectively, of the compound.

However, equation (10) can be simplified as the heat of formation of the gaseous compound from the elements in their standard states, $Q_f^{st}(g)$, is given by

$$Q_f^{st}(g) = Q_f^a(g) - \sum Q_{st}^a(E) \qquad (11)$$

Substituting equation (11) into equation (10) gives

$$Q_f^\circ = Q_f^{st}(g) - L_v - L_f \qquad (12)$$

$Q_f^{st}(g)$ can be calculated for a given compound from its molecular formula, i.e. summation of the bond energies

$$Q_f^{st}(g) = \sum Q^{st}(b) + Q_R + Q^{st}(X{-}NO_2) \qquad (13)$$

where $\Sigma Q^{st}(b)$ is the sum of the bond energies, Q_R is a correction for resonance stabilization and Q^{st} (X–NO_2) is the energy of the energetic group. In the case of polyGLYN, X is the oxygen atom of the nitrate ester moiety. The difficulty with equation (12) is that, for new energetic materials, values of L_v and L_f are not often known. In such instances they are estimated by using values of analogous materials. This is not a serious drawback to the calculation because the sum of these terms is much less than the magnitude of $Q_f^{st}(g)$. The sum of L_v and L_f is estimated to be between -12 and $-18\,\text{kcal mol}^{-1}$, depending on the molecular weight of the polymer, for the POWA series of nitrate ester materials. (Note that the thermochemical convention for explosive calculations is that endothermic changes are treated as negative and exothermic changes as positive.) For polyGLYN, Q_f° is calculated as $61.3\,\text{kcal mol}^{-1}$.

Returning to equation (8), the $\Sigma Q_f^{st}(x)$ term is more difficult to calculate mainly because the products of explosion vary, for example, oxygen atoms may be distributed as CO_2, CO, H_2O and O_2. This problem was addressed by Kistiakowsky and Wilson[13], who applied thermodynamic and kinetic data to a system '... a time, shortly after detonation, after most of the external work has been done but while the gases are still hot.' They drew up a set of rules to predict the distribution of the products. The Kistiakowsky and Wilson (K–W) rules are as follows.

1. Permissible products—only the following molecules (and no free atoms) can appear in the explosion products: C_{amorph}, CO, CO_2, H_2, H_2O, O_2, N_2.
2. Distribution of oxygen—(a) the C is first oxidized to CO; (b) any residual oxygen the oxidizes the H to H_2O; (c) any residual oxygen then oxidizes the CO to CO_2; (d) any residual oxygen then separates as O_2.

As the empirical formula of polyGLYN is $C_3H_5NO_4$ and applying the K–W rules, the products of explosion are

$$C_3H_5NO_4 = 3CO_{(g)} + H_2O_{(g)} + 3/2H_{2(g)} + 1/2N_{2(g)} \tag{14}$$

thus $\Sigma Q_f^{st}(x) = (3 \times 26.39) + 57.8 = 136.97\,\text{kcal mol}^{-1}$.

Using equation (8), $Q_x = 75.7\,\text{kcal mol}^{-1} = 316.7\,\text{kJ mol}^{-1} = 2661\,\text{kJ kg}^{-1}$.

This is the figure which indicates the energy of a compound. Comparison of this figure with those calculated for polyNIMMO, $818\,\text{kJ kg}^{-1}$, and for GAP, $2500\,\text{kJ kg}^{-1}$, shows that polyGLYN is expected to be significantly more energetic than polyNIMMO and marginally more so than GAP. Of course, it must be remembered that the calculated value may differ from experimental results and this may be because the theoretical energy of the binder is not fully released during an explosion as well as due to errors in the experiments or inaccuracies in the assumptions made in the calculations. Nevertheless, Q_x is an important value in assessing the energy and, indirectly, the safety of energetic materials.

More directly, polyGLYN is not in the UN Class 1 (high explosive) category[14]. Other properties, such as viscosity which affects ease of handling during formulation, are listed in *Table 1*.

Conclusions

A novel α,ω-hydroxytelechelic energetic polymer, known as poly(glycidyl nitrate), polyGLYN or POWA3, for use in propellants and explosive compositions has been prepared. It has molecular weights in the range 500–3500; may be di- or trifunctional; is free of cyclic oligomer and monomer contamination; has a narrow molecular weight distribution; has a T_g of $-35°C$, and its energy (i.e. theoretical heat of explosion, Q_x), $2661\,\text{kJ kg}^{-1}$, is of the same order as that of trinitrotoluene (TNT).

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