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Energetic polymer subjected to high energy radiation

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Abstract

PolyNIMMO is regarded as an energetic polymer. It consists of a nitrated ester group and an ether linkage. When polyNIMMO is subjected gamma radiation up to doses of 250 kGy there is no evidence of degradation, however, at higher levels of gamma radiation up to 750 kGy structural changes in the polyNIMMO backbone were observed [Polymer 44 (2003) 7617–7624]. These observations were based on polyNIMMO which was gamma irradiated in the bulk phase [Polymer 44 (2003) 7617–7624; Polymer 42 (2001) 7711–7718]. The results presented in investigation are from polyNIMMO which has been irradiated in solution. PolyNIMMO dissolved in halogenated and aromatic solvents was found to undergo structural changes when subjected to doses of gamma radiation up to 250 kGy. An increase in molecular weight and glass transition temperature was observed with the formation of water and an aldehyde. End chain linking together with hydrogen abstraction of the pendant methyl group were the two suggested reaction schemes.

Keywords: Energetic polymers; Gamma radiation; PBXs

1. Introduction

PolyNIMMO was developed for the use in polymer bonded explosives. It is an energetic polymer which is used to bind explosives crystals, increasing the explosive performance, without compromising its vulnerability to accidental initiation. PolyNIMMO [poly (3-nitratomethyl-3-methyloxetane)] consists of a nitrated ester group and an ether linkage [3] as shown in Fig. 1. The results from thermal studies show that the prepolymer polyNIMMO ages naturally with time, even at ambient temperature, and that decomposition is accelerated by an increase in temperature [2,4–7]. The results from gel permeation chromatography (GPC) show that thermally aged polyNIMMO undergoes chain scission and crosslinking. The results from infrared (IR) and nuclear magnetic resonance spectroscopy (NMR) show the presence of a carbonyl group in a formate ester. The formate ester is produced when a proton is abstracted from a methylene carbon in the polymer backbone resulting in a carbon radical which in turn is oxidised giving an unstable oxy radical. The adjacent C–C atoms then undergoes bond scission resulting in a formate ester as well as an alkoxy radical, as shown in Fig. 2 [7].

IR spectroscopy also shows the presence of an N–O peak at 1550 cm^{-1} in thermally aged polyNIMMO. The loss of a nitroxide radical is said to be responsible for the peak [7]. This radical then reattaches itself to a newly created radical site on the polymer backbone as shown in Fig. 3.

The results from gamma radiation [1] show that polyNIMMO is very stable to gamma radiation up to doses of 250 kGy. Although radicals are produced at this level and lower levels of radiation they are short-lived and do not cause structural changes in polyNIMMO. At higher levels of radiation up to 750 kGy structural changes took place. Here, the presence of an aldehyde group and format ester were observed in the NMR spectra, and peaks due to a carbonyl group and water were also seen in the IR spectra. The results from the GPC show no change in the molecular weight. The suggested mechanism for degradation of polyNIMMO by gamma radiation is shown in Fig. 4. Here, a hydrogen atom is abstracted at the methyl carbon site. Oxygen then attaches itself to the radical resulting in peroxidation. The peroxide rearranges itself to give an aldehyde and water as a by-product.

The work discussed above consisted of gamma irradiating polyNIMMO in the bulk phase. Here, the molecular

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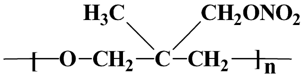


Fig. 1. Molecular structure of polyNIMMO.

chains are arranged in a tight coil of tangled mass which hinder the penetration of gamma rays. In order to increase the penetration of gamma rays and to increase the hydrodynamic volume of the polymer, polyNIMMO was dissolved in suitable solvents before being irradiated. The results are presented in this paper.

2. Experimental

PolyNIMMO was obtained from MOD. In order to remove any residual dissolved gases that may have been present due to natural ageing, as well as any reactants from the synthesis process, the prepolymer polyNIMMO was dried then degassed for several hours by applying a vacuum. Solutions were made containing polyNIMMO dissolved in tetrahydrofuran, dichloroethane, dioxan, dichloromethane, trichloromethane, tetrachloromethane, benzene, toluene and xylene. The solutions were placed into 20 ml Chromacol glass vials. The vials were then capped and sealed in air. All the vials containing polyNIMMO were irradiated using a ^{60}Co as a source of high-energy gamma radiation.

IR analyses of the samples using an attenuated internal reflection apparatus were carried out using a Perkin–Elmer 983 Infrared Spectrophotometer.

GPC was carried out to determine the molecule weight of the samples using a Viscotek Size Exclusion Chromatography (SEC) unit. The viscotek pump was coupled to a Waters auto sampler and refractive index detector using Millennium software for data collection and processing. The GPC was calibrated using polystyrene samples supplied by Polymer Laboratories. The calibration standards had a range of molecular weights from 580 to 283.300 Mp with an average M_w/M_n of 1.02.

A Bruker DPX250 (250 MHz) NMR spectrometer was used to produced H^1 and C^{13} NMR spectra of polyNIMMO, and a Mettler DSC 30 with RT11 Processor was used to determine the glass transition temperatures.

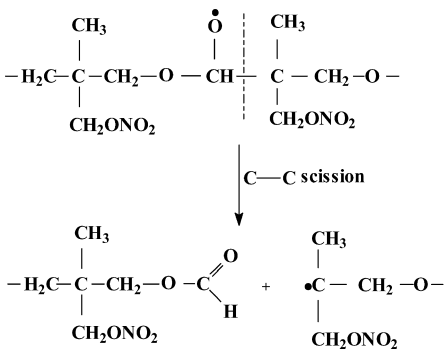


Fig. 2. Mechanism for the chain scission of polyether backbone for thermally aged polyNIMMO.

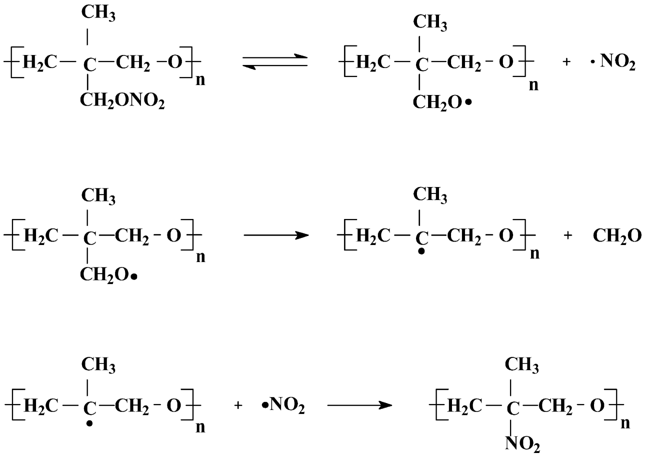


Fig. 3. Mechanism for the homolytic scission of the O–NO$_2$ bond for thermally aged polyNIMMO.

3. Results and discussion

PolyNIMMO samples dissolved in 10% solutions of tetrahydrofuran, dichloroethane and dioxan were irradiated in air and nitrogen atmospheres to a total dose of 50 kGy. The solvent was then allowed to evaporate from the samples and the samples placed in a vacuum oven to remove any residual solvent. In order to see if there has been a change in the molecular weight of irradiated polyNIMMO, GPC was carried out on the samples. The results are presented in Fig. 5. From Fig. 5 it can be seen that the molecular weight of irradiated polyNIMMO dissolved in tetrahydrofuran and dioxan did not increase significantly compared to polyNIMMO irradiated in dichloroethane. Here, the molecular weight was seen to increase by $\sim 30\%$ when in a nitrogen atmosphere. This increase in molecular weight is probably due to the polyNIMMO and chlorine atoms both forming radicals when gamma irradiated. The extra radicals formed from the chlorinated solvent reacts with the polyNIMMO, resulting in an increase in molecular weight. In an air

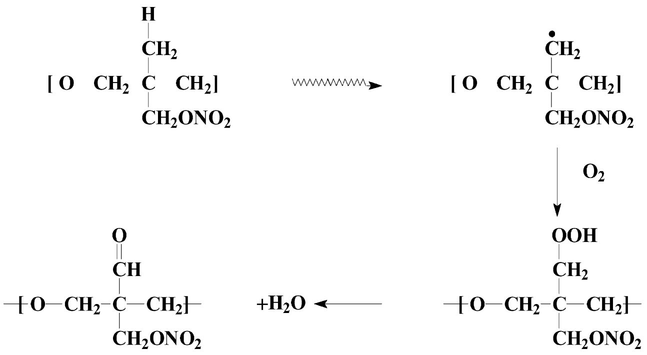


Fig. 4. Proposed mechanism for the formation of an aldehyde group by side chain peroxidation

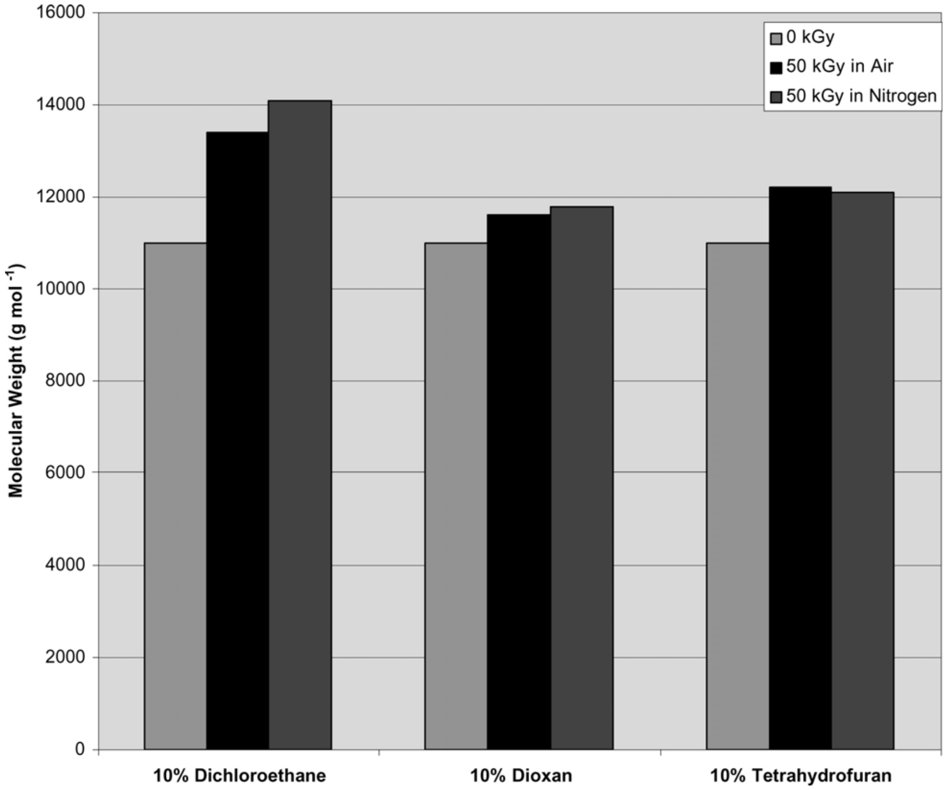


Fig. 5. Molecular weight values from GPC of polyNIMMO dissolved in 10% dichloroethane, 10% dioxan and 10% tetrahydrofuran, irradiated to 50 kGy.

environment, the molecular weight was found to only increase by ~22%. This is probably due to the oxygen in the air acting as a radical scavenger and competing with the polyNIMMO for the free radicals.

PolyNIMMO has been found to produce radicals when irradiated in dichloromethane and other chlorinated solvents. In order to increase the production of radicals polyNIMMO was dissolved in 10% solutions of dichloromethane, trichloromethane, and tetrachloromethane. These samples were subjected to gamma irradiation up to 250 kGy. The solvent was allowed to evaporate from the samples and the samples placed in a vacuum oven to remove any residual solvent. In order to see if there has been a change in the molecular weight of irradiated polyNIMMO, GPC was carried out on the samples. The results are presented in Fig. 6(a). From Fig. 6(a), it can be seen that the molecular weight of polyNIMMO dissolved in dichloromethane has increased by 12 times for doses over 50 kGy, whereas the molecular weight of polyNIMMO dissolved in trichloromethane has increased by 15 times and is still seen to be increasing. This result is to be expected since trichloromethane contains more chlorine atoms than dichloromethane which results in more radicals being produced. These radicals then react with the polymer resulting in an increase in molecular weight. On the other hand, there was no real significant change in the molecular weight of polyNIMMO irradiated in tetrachloromethane. This result suggests that the excess chlorine radicals are reacting with each other rather than the polymer.

In order to see if the increase in molecular weight of irradiated polyNIMMO was dependent upon concentration 1, 5, and 10% solutions of polyNIMMO dissolved in dichloromethane were subjected to gamma irradiation up to 250 kGy. The solvent was allowed to evaporate from the samples and the samples placed in a vacuum oven to remove any residual solvent. In order to see if there has been a change in the molecular weight of irradiated polyNIMMO, GPC was carried out on the samples. The results are presented in Fig. 6(b). These results show that as the concentration of the polyNIMMO increases, its molecular weight also increases when irradiated to doses over 50 kGy. The increase in molecular weight is due to the ends of the polymeric chains linking together. Concomitantly a solution, which contains a higher concentration of polymer, would have a higher degree of chain ends, thus resulting in a higher molecular weight after gamma irradiating.

It can be observed from the results so far, that dissolving polyNIMMO in a solvent greatly increases its susceptibility to gamma radiation. The presence of chlorine enhances the degree of radicals which in turn react with the polymer resulting in an increase in molecular weight, however, too many chlorine radicals can have the opposite effect. The majority of solvents do produce radicals to a greater or lesser extent when subjected to gamma radiation which can then react with the polyNIMMO. In order to eliminate the solvent effect aromatic solvents were explored, since they have the ability to hold on tightly to their electrons through resonance stabilisation.

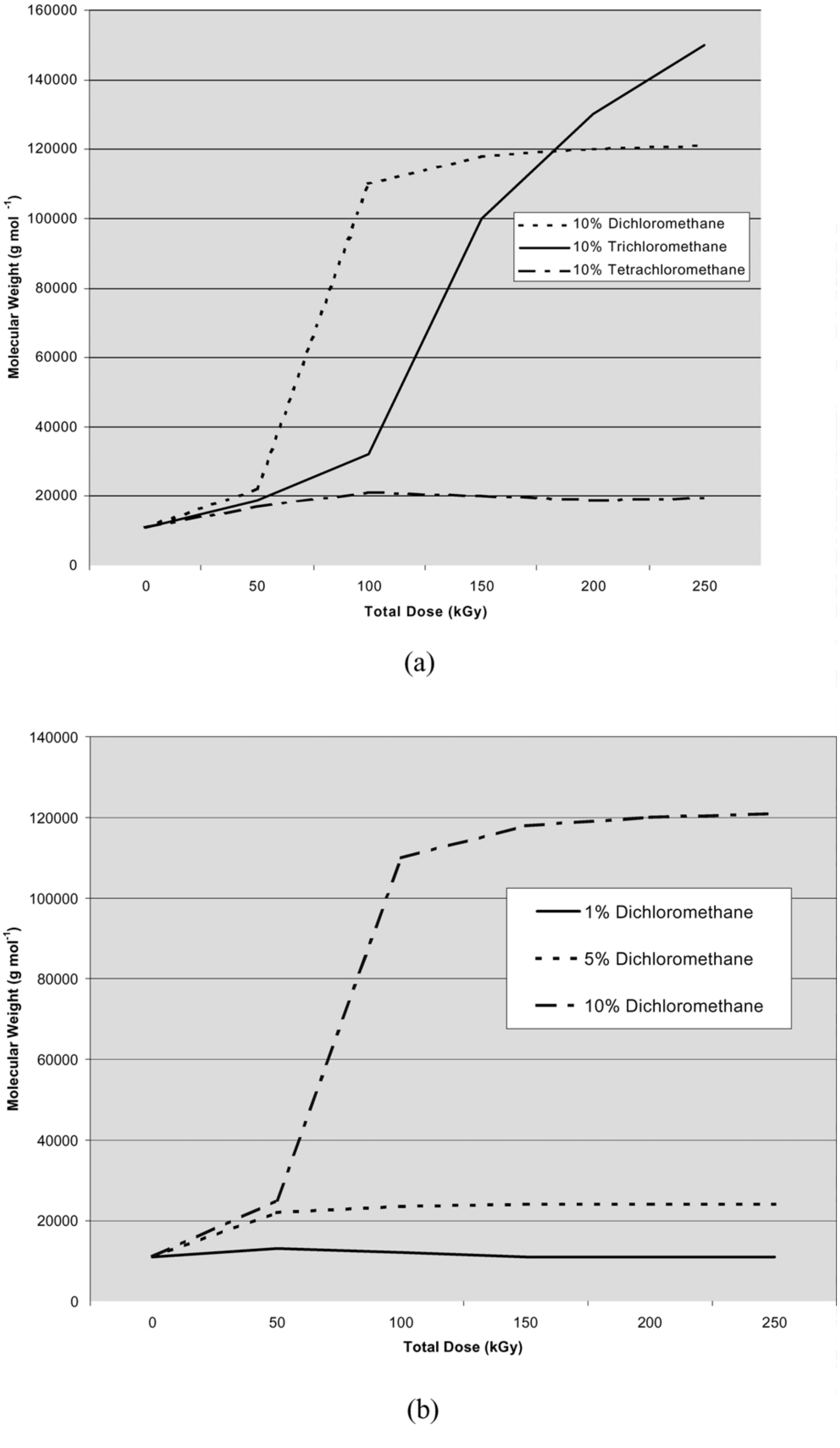
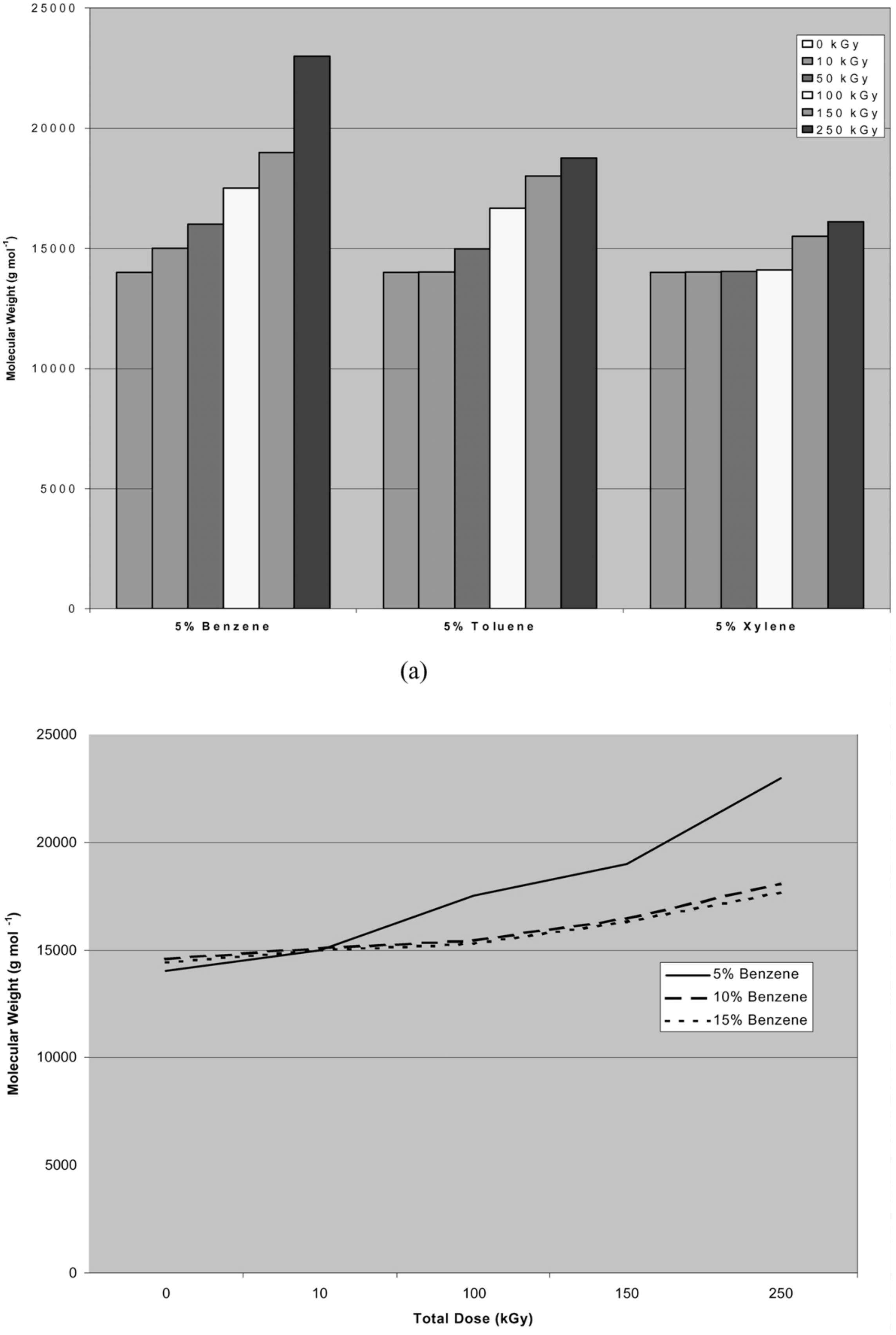


Fig. 6. Molecular weight values from GPC of polyNIMMO dissolved in (a) 10% dichloromethane, 10% trichloromethane and 10% tetrachloromethane, and (b) 1, 5 and 10% dichloromethane irradiated to 250 kGy.



(a)

(b)

Fig. 7. Molecular weight values from GPC of polyNIMMO irradiated to 250 kGy dissolved in (a) 5% benzene, 5% toluene and 5% xylene, and (b) 5, 10 and 15% benzene.

PolyNIMMO was dissolved in 5% solutions of benzene, xylene and toluene, and were irradiated to a total dose of 250 kGy. The solvent was allowed to evaporate from the samples and the samples placed in a vacuum oven to remove any residual solvent. In order to see if there has been a change in the molecular weight of irradiated polyNIMMO, GPC was carried out on the samples. The results are presented in Fig. 7(a). It can be seen from Fig. 7(a) that the molecular weight for irradiated polyNIMMO dissolved in benzene has increased by 1.5 times, which is quite low compared to the chlorinated solvents which gave a far higher value. The increase in molecular weight of polyNIMMO was observed to be dependent on the degree of gamma radiation for all aromatic solvents used in this investigation. The solvent benzene resulted in the highest increase in molecular weight for irradiated polyNIMMO followed by toluene then xylene. When polyNIMMO dissolved in benzene is subjected to gamma radiation the majority of radicals are formed on the polymer backbone through hydrogen abstraction, resulting in an increase in molecular weight. However, when toluene or xylene is used as the solvent and subjected to gamma radiation, the radicals formed by hydrogen abstraction predominantly occurs in the solvent through the pendant methyl groups. These radicals do not react with the polymer since they are held tightly in the aromatic structure. Fewer radicals are therefore formed on the polymer backbone resulting in a reduced increase in molecular weight.

In order to see if the increase in molecular weight of irradiated polyNIMMO was dependent upon the concentration 5, 10 and 15% solutions of polyNIMMO dissolved in benzene were irradiated to a total dose of 250 kGy. The solvent was then allowed to evaporate from the samples and the samples placed in a vacuum oven to remove any residual solvent. In order to see if there has been a change in the molecular weight of irradiated polyNIMMO, GPC was carried out on the samples (see Fig. 7(b)). From Fig. 7(b) it can be seen that the molecular weight of irradiated polyNIMMO surprisingly increases with decreasing concentration. Assuming that all the radicals are formed on the polymer this result may be due to the increase in hydrodynamic volume of the polymer leading to an increase in penetration of the gamma rays.

To investigate if any structural changes had occurred IR and NMR spectroscopy were carried out on 5% polyNIMMO dissolved in benzene which had been gamma radiated up to 250 kGy. The IR and NMR spectra are presented in Figs. 8 and 9, respectively. It can be seen from Fig. 8 that a carbonyl peak at 1729 cm^{-1} is present for samples which have been irradiated to 100 kGy and above. At 250 kGy there is evidence of a free water peak at 3443 cm^{-1}. In order to determine the functional species which contains the carbonyl group (i.e. aldehyde, ketone etc.), the irradiated samples were immersed in Tollens reagent. The results indicated the presence of aldehyde groups. From the NMR spectra shown in Fig. 9, no major structural changes were observed for polyNIMMO which had been irradiated up to 250 kGy. However, a doublet was observed at 9.6 ppm, with a smaller peak appearing at 8.1 ppm as shown in Fig. 9c. These peaks were probably due to the presence of an aldehyde and format ester group.

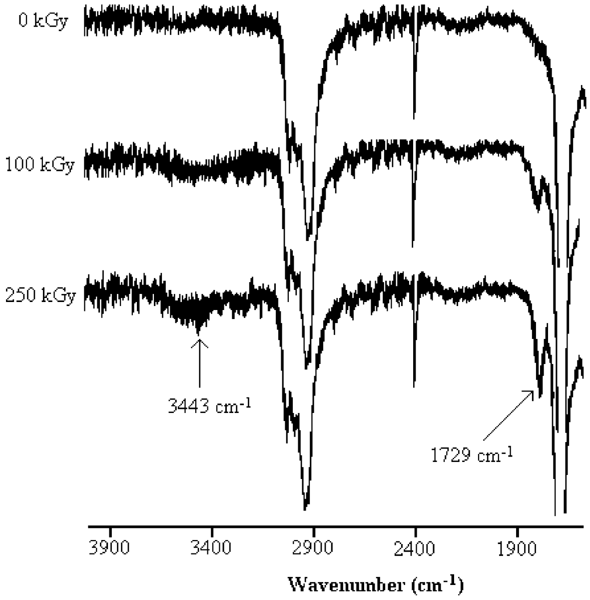


Fig. 8. IR spectrum of polyNIMMO irradiated to 250 kGy.

In order to see if there had been a change in molecular mobility, the glass transition temperature was determined from DSC thermograms. DSC was carried out on polyNIMMO which was dissolved in 1% solution of benzene and irradiated to a total dose of 250 kGy. The results are presented in Fig. 10. The glass transition temperature was found to increase with increasing radiation dose suggesting that the mobility of the polymeric chains have indeed decreased which is probably due to the increase in molecular weight.

4. Conclusions

When polyNIMMO in its bulk form is subjected to gamma radiation, structural changes were only observed to take place when radiation doses reached 750 kGy and higher [1]. However, when polyNIMMO was dissolved in suitable solvents structural changes took place at much lower doses, i.e. >50 kGy. Dissolving a polymer in a suitable solvent is known to increase its hydrodynamic volume. The polymeric chains are allowed to uncoil resulting in a larger surface area thus making it more susceptible to gamma irradiation. Irradiating polyNIMMO in chlorinated solvents resulted in a large increase in molecular weight due to the chlorine radicals interacting with the polymer. The molecular weight was also found to increase with increasing concentration of the chlorinated solutions. However, if the number of chlorine radicals was too high (ie using tetrachloromethane as a solvent) the

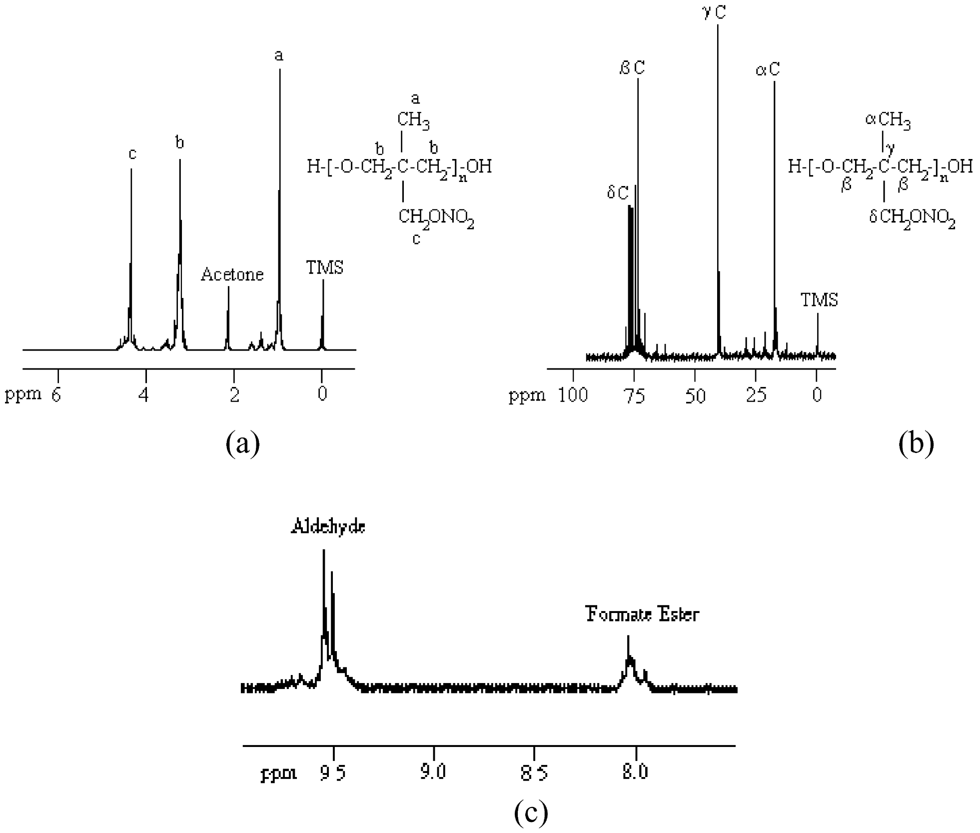


Fig. 9. (a) H^1 and (b) C^{13} NMR spectrum of polyNIMMO dissolved in 5% benzene and irradiated to 250 kGy and (c) H^1 NMR spectra of polyNIMMO dissolved in 5% benzene and irradiated to 250 kGy.

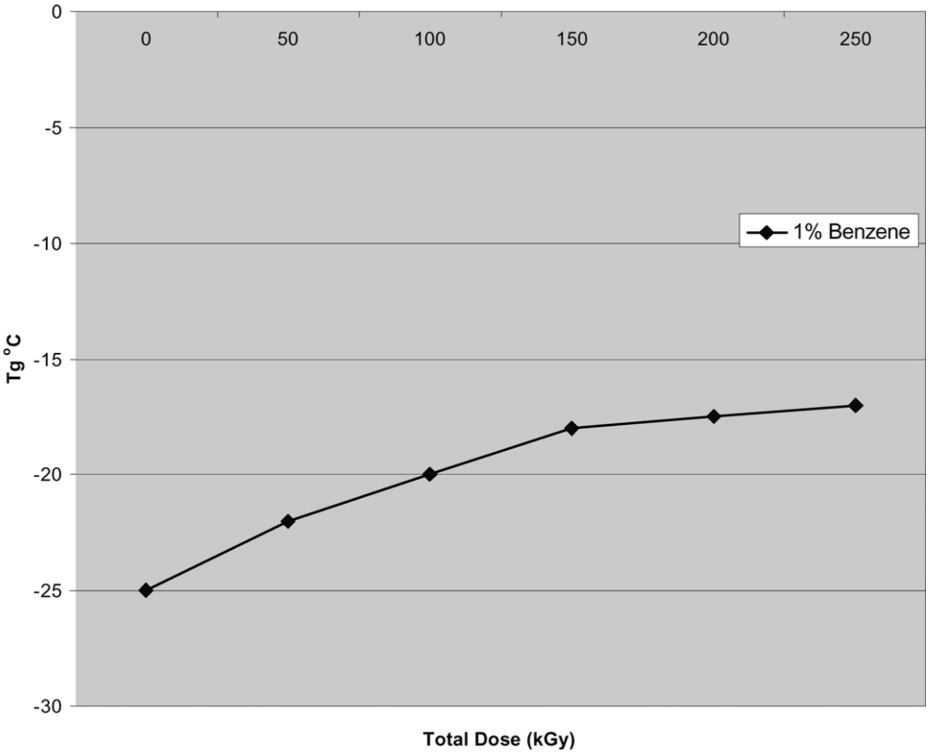
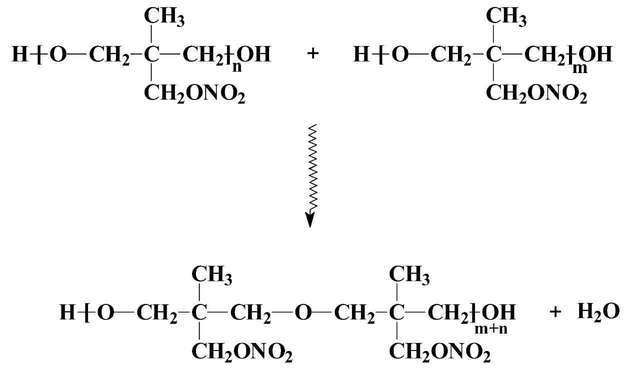


Fig. 10. Glass transition temperatures of polyNIMMO dissolved in 1% benzene and irradiated to 250 kGy.



$$H{+}O{-}CH_2{-}\overset{CH_3}{\underset{CH_2ONO_2}{C}}{-}CH_2{+}_nOH \;+\; H{+}O{-}CH_2{-}\overset{CH_3}{\underset{CH_2ONO_2}{C}}{-}CH_2{+}_mOH \longrightarrow H{+}O{-}CH_2{-}\overset{CH_3}{\underset{CH_2ONO_2}{C}}{-}CH_2{-}O{-}CH_2{-}\overset{CH_3}{\underset{CH_2ONO_2}{C}}{-}CH_2{+}_{m+n}OH \;+\; H_2O$$

Fig. 11. Proposed mechanism for the chain end linking of polyNIMMO.

molecular weight of the irradiated polyNIMMO only slightly increased. Here, the radicals are probably reacting with each other rather than the polymer.

Irradiation of polyNIMMO in aromatic solvents also led to an increase in the molecular weight of the polymer. As expected the increase in molecular weight was not as great as the values observed for the chlorinated solvents, because the radicals formed from radiating the aromatic solvents remained within the solvent molecule. Introducing pendant methyl side groups to the aromatic ring resulted in a reduced increase in molecular weight of irradiated polyNIMMO, because the gamma radiation preferred to attack the hydrogen on the aromatic methyl groups rather than the polymer.

When polyNIMMO was irradiated in benzene, the lowest concentration (1%) gave the largest increase in molecular weight. It is assumed that as the concentration of the solution decreases to 1% there is an increase in the penetration of gamma rays resulting in more radicals being formed on the polymer backbone, leading to an increase in molecular weight of the polymer. However, the contrary occurs for polyNIMMO dissolved in chlorinated solvents. Radiating chlorinated solvents produces an abundance of radicals which can react with the polymer. Increasing the concentration of the polymer simply provides more sites for the chlorinated radicals to interact, resulting in an increase in molecular weight of the polymer.

The results from NMR suggest that very little structural changes have taken place. A small doublet was observed at 9.6 ppm, with a smaller peak appearing at 8.1 ppm due to the presence of an aldehyde and format ester group. The formation of an aldehyde group was also seen in the IR spectra, together with a peak resulting from the presence of water. The suggested mechanism is shown in Fig. 4. However, this mechanism does not result in an increase in molecular weight therefore another process must also be taking place. The results from the GPC, DSC and IR analyse showed an increase in the molecular weight, reduced molecular mobility and the presence of water. The higher molecular weight material always remained in solution therefore suggesting that cross-linking has not taken place. The mechanism proposed for the increase in molecular weight is shown in Fig. 11. Here, the radicals are formed on the ends of the chains resulting in the polymeric chains linking together with the formation of water as a by-product.

Acknowledgements

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