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NMR study of the effect of electron beam processing on a poly(ether-*block*-amide)

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Abstract

^{1}H T_1 and $T_{1\rho}$ measurements together with FID function fitting were used to investigate the effect of electron beam irradiation on the dynamics of a poly(ether-*block*-amide). Rigid polyamide and mobile polyether phases are seen in the FID of the control polymer. Irradiation causes a decrease in mobility of the mobile phase. Spin diffusion evident in the T_1 and $T_{1\rho}$ shows qualitatively a phase separated morphology on the 2 nm scale and prevents a clear interpretation of the changes caused by irradiation. Only minor differences were seen in the ^{13}C CPMAS NMR spectra of the control and irradiated polymers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Relaxation; Radiation; Poly(ether-amide)

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1. Introduction

Poly(ether-*block*-amides) are thermoplastic elastomers consisting of rigid polyamide segments and flexible polyether segments [1]. One common polymer is the block copolymer between polyethylene oxide as the ether and nylon-12 as the polyamide, P(EO,N12) (**I**), which has found application in angioplasty balloon technology [2].

$[\text{–}(CH_2CH_2O)_{6.0}\text{–}(C(O)(CH_2)_{11}NH)_{1.0}\text{–}]$ (**I**)

In order for poly(ether-*block*-amide) to be used in medical applications it is essential that its properties are not compromised by sterilisation using ionising irradiation. In principle, radiation damage can result in both chain scission and cross-linking. Extensive chain scission will lead to a reduction in the molar mass while cross-linking increases the molar mass leading to a less flexible product [3]. Consequent on these changes induced crystallisation or the destruction of crystalline regions can take place. Previous work on polyethylene oxide has established that chain scission predominates when electron beam irradiation is carried out in air whilst cross-linking predominates when irradiated in vacuum [4]. Cross-linking has been proposed as the main consequence of damage in polyamides [3], leading to the loss of crystallinity. Significant levels of either chain scission or cross-linking is likely to have a deleterious effect on the physical properties of P(EO,N12). The precise physical properties of poly(ether-*block*-amide) polymers will depend on the nature of the polyamide and polyether segments as well as the percentage composition. In fact, little work has been published on the structure and detailed morphology of this family of polymers. However, the general expectation is of a high degree of phase separation between the flexible polyether and rigid polyamide segments. Thus, in one study of a poly(ether-*block*-amide), with 58 wt% polyethylene oxide, crystallisation of the polyamide segments was seen to a level roughly 80% of that seen in the homopolymer while the polyether segments remained largely amorphous despite poly(ethylene oxide) forming a well established crystalline phase, at best a crystalline content of 20% of the homopolymer case [5]. Moreover, the structure of the crystalline polyamide phases appeared to be identical to the thermodynamically stable structure seen in the corresponding homopolymer. The aim of work reported here was to determine the effect of radiation damage on a sterilised angioplasty balloon made from Atofina PEBAX 7033, a grade, which has a significantly lower polyether content. ^{1}H NMR relaxation times were determined to assess changes in the polymer dynamics resulting from irradiation and high resolution ^{13}C NMR was used to look for changes in the chemical structure.

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2. Experimental

2.1. Materials

Poly(ether-*block*-amide) was obtained from Atofina (PEBAX 7033) with a composition 89.3 wt% polyamide and 10.7 wt% polyethylene oxide. The polymer balloon was manufactured using a proprietary procedure by AVE. Three samples were studied, one a control was not irradiated, two others were treated by 46 kGy radiation once and twice, respectively.

2.2. Solid state NMR

The ^{1}H and ^{13}C NMR spectra were acquired on a Bruker MSL200 NMR spectrometer operating at 200.13 and 50.32 MHz, respectively. A solid echo pulse [6] sequence $[(\pi/2)_y - t_1 - (\pi/2)_x - t_2]$, combined with phase cycling and an echo delay of 8 μs, was used together with a pulse width of 3.0 μs to obtain the free induction decay (FID). T_1 was measured using the saturation recovery method in a single point acquisition manner, collecting 256 points with a time increment of 10 ms. The $T_{1\rho}$ decay was similarly obtained by single point acquisition with 256 points and a time increment of 200 μs for the spin-locking pulse. The RF amplitudes and phase orthogonality were checked prior to data acquisition using a standard multiple pulse tune up procedure on a H_2O sample. Four thousand data points were acquired for the FID with a dwell time of 0.5 μs to ensure a faithful reproduction of the fast decaying component. Typically, the sample was left to equilibrate for 1 h before collecting 32 transients. A value of t_2 was chosen to ensure that data acquisition began on the top of the solid echo. Experimental errors for use in the T_1, and $T_{1\rho}$ relaxation time analysis as well as the FID analysis were estimated from the last 20 data points of the appropriate data set. Non-linear least-squares fitting based on the Levenberg–Marquardt algorithm [7] was used to extract the ^{1}H relaxation times from the appropriate decay curve and to function fit the FID.

High resolution ^{13}C NMR spectra were obtained using magic angle spinning (MAS) and high power proton decoupling [8]. In certain experiments aimed at selecting particular phases cross-polarisation was also employed. Phase selection based on $T_{1\rho}$ differences was achieved by the delayed contact pulse experiment where the contact pulse on the ^{13}C spins is delayed until all the magnetisation associated with the shorter $T_{1\rho}$ component has decayed away, in this way only the phase with the long $T_{1\rho}$ will be seen. Variations in T_2 were exploited by delaying the spin-locking pulse in a ^{13}C cross-polarisation experiment for a time of the order of five times the T_2 of the fastest decaying signal giving only the phase with a long T_2.

3. Results and discussion

Various functional forms can be used to represent the components in the FID of a polymer and although rigorous forms can be presented for idealised homopolymers [9,10], no such forms exist for complex multiphasic copolymers. Consequently, for the most part FID fitting is based on an empirical choice of function. The choice of function can, however, be rationalised in terms of the dynamical behaviour of the phase. Accurate fitting of the ^{1}H FID of the amorphous nylon-12 and poly(ether-*block*-amide) to an exponential, gaussian and Weibullian function proved to be straightforward, see Table 1. In the limit of the exponent α in the Weibull function being equal to unity, the function reduces to an exponential, hence all the ^{1}H FID's were well represented by a gaussian and exponential functions. The ^{1}H T_1 and $T_{1\rho}$ derived from the saturation recovery and relaxation decay curves are shown in Table 2. All the FID and T_1 fits were statistically acceptable as were the $T_{1\rho}$ except for the 1 × irradiated poly(ether-*block*-amide), $T_{1\rho}$.

The ^{1}H FID for amorphous nylon-12 is well described by a simple gaussian decay with a T_2 of 10.8 μs. Both the gaussian nature of the function and the T_2 value suggest the absence of high frequency large amplitude motions, typical of an amorphous polymer below its glass transition temperature, T_g. Thus, a gaussian form for the FID is expected for a powder distribution of rigid dipolar interactions in a multi-spin system [11]. Oscillatory terms are seen when the polymer is highly crystalline, as in an Abragam or dipolar function [10], and their absence is consistent with the material being amorphous. Further, the time

Table 1
Function fitting of the ^{1}H FID

	Gaussian		Exponential		Weibull		
	F	T_2 (μs)	F	T_2 (μs)	F	T_2 (μs)	α
Nylon-12	0.99	10.8	–	–	0.01	83.2	1.391
Control	0.61	11.5	0.09	382	0.33	22.4	1.000
1 × irradiated	0.73	11.3	0.04	156	0.25	21.4	1.000
2 × irradiated	0.72	10.9	0.05	141	0.24	21.7	1.000

Table 2
^{1}H T_1 and $T_{1\rho}$

	T_1		$T_{1\rho}$	
	F	T_1 (s)	F	$T_{1\rho}$ (ms)
Nylon-12	1.0	0.49	0.36	2.2
			0.64	8.6
Control	1.0	0.39	0.39	2.2
			0.61	9.1
1 × irradiated	1.0	0.44	0.21	0.8
			0.55	2.8
			0.24	9.0
2 × irradiated	0.17	0.10	0.11	0.5
	0.79	0.46	0.50	2.4
			0.39	9.9

constant for the gaussian, $T_2 = 10.8$ μs, although somewhat larger than expected for the rigid lattice second moment for the ^{1}H spins is still indicative of the absence of any large amplitude motions. ^{1}H NMR experiments on nylon-6.6, where the polymer dynamics are somewhat more restricted than in nylon-12, suggest a rough halving in the second moment from a rigid lattice value of $22G^2$ to $12G^2$ at room temperature [12], which would correspond to an increase in T_2 from the rigid lattice value of ca. 7.5 μs to the observed 10.8 μs. In fact, this reduction in the second moment corresponds to a 40° amplitude rotational oscillation. Similar values were seen in a ^{1}H NMR study of amorphous nylon-6.6, where 18° librational motion was superimposed on a 15° internal rotation jump [13]. In contrast, the FID's for the three P(EO,N12) samples show a more complex functional form, as can be seen in Fig. 1, with a range of T_2 values as might be expected for a phase separated polymer where the constituent phases present show a difference in mobility. Note that phase information will only be obtained if the FID component can be associated with the different phases as opposed to molecular entities, through the combined use of selective ^{13}C NMR and spin diffusion, Goldman–Shen [14] or dipolar filter [15], experiments. As in the case of amorphous nylon-12 the gaussian functions with short T_2 can be identified with a rigid polymer, well below its T_g. Equally straightforward to understand is the exponential with a long T_2, this represents highly mobile polymer, well above its T_g. The fraction with an exponential form but a short T_2 is less easily understood. Empirically, the value for the T_2 indicates a polymer, which is only a little less rigid than the major component and yet this is not reflected in the functional form. Often a amorphous polymer will show a change in functional form as it approaches its T_g in such a way that it can be best described by a Weibull function with an exponent, α, lying between 1 and 2. Despite the fitting procedure allowing this, the best fit was found when $\alpha = 1.000$. Although the question remains about the true functional form, it is clear that the short T_2 exponential represents polymer in a relatively rigid environment.

Selective ^{13}C NMR experiments were carried out with the aim of establishing qualitatively the chemical identity of the components seen in the ^{1}H FID. A reference ^{13}C cross-polarisation MAS NMR spectrum of the control poly(EO,N12) balloon is shown in Fig. 2a. Amide segment resonance, 44–20 ppm, is clearly present while the intensity of the polyether segments at 71.3 ppm are attenuated from the intensity one might have expected on the basis of the relative mass fractions owing to the greater mobility of the ether segments. Clearer selection of the mobile phase can be made by adding a delay before spin-locking the ^{1}H magnetisation. During this delay, the ^{1}H signal will decay by T_2 relaxation and by choosing an appropriate delay all the ^{1}H magnetisation associated with the short T_2 component can be removed. Based on the time constant of 11.5 μs found for the gaussian decay in the ^{1}H FID a T_2 relaxation delay of 30 μs was used. With this delay, the contribution from the rigid gaussian component will be negligible. In this selective ^{13}C NMR spectrum, Fig. 2b, the intensity of the amide carbonyl at 174 ppm is reduced with respect to the polyether methylene at 71.3 ppm. Significantly, though, not all of the amide intensity is lost demonstrating that some of the amide segments must contribute to the exponential components in the ^{1}H NMR FID. A complication to the interpretation of this data is that spin diffusion, which occurs during the spin-lock will blur the distinction between phases. Attempts to identify specifically the long T_2 exponential component by using a 100 μs T_2 relaxation delay were unsuccessful as no cross-polarisation signal was seen. Unique identification of the short T_2 component is not possible owing to the

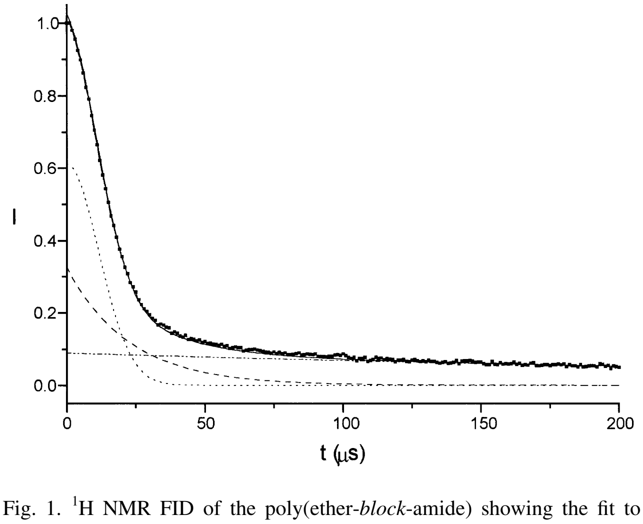

Fig. 1. ^{1}H NMR FID of the poly(ether-*block*-amide) showing the fit to gaussian and exponential functions. The individual experimental points are shown while the solid line represents the sum of the fitted gaussian, Weibullian and exponential functions. The gaussian function is shown by a dotted line, the Weibullian by a dashed line and the exponential by the dotted and dashed line.

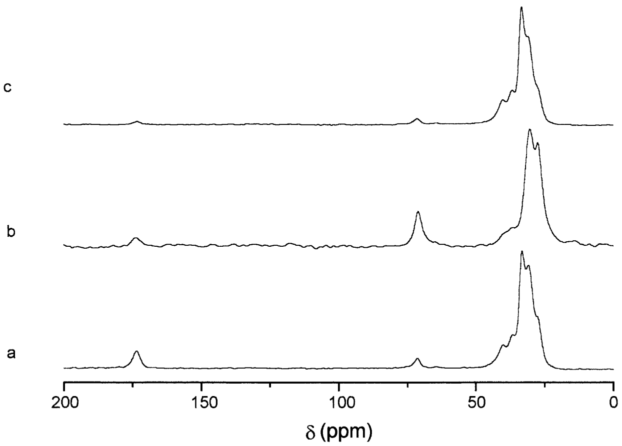

Fig. 2. ^{13}C CPMAS NMR spectra of the control poly(ether-*block*-amide): (a) normal CP contact time 1 ms, recycle delay 3 s; (b) delayed spin-lock CP with a delay time of 30 μs and a contact time of 1 ms; (c) short contact time, 50 μs, CP, with a recycle delay of 3 s.

similarity in the T_2 for the short T_2 exponential and gaussian components. However, a short contact time ^{13}C CPMAS NMR spectrum, $t = 50\ \mu$s, shown in Fig. 2c, will be biased towards the gaussian component. Here the ether methylene resonance is attenuated with respect to the amide methylene, but still present. Despite the complications arising from the imperfectly selective nature of the experiments, the overall impression is that the ^{1}H gaussian and short T_2 exponential signals arise predominantly from polyamide segments with some contribution from polyether. Conclusions about the nature of the segregation of these amide and ether segments cannot be drawn since T_2 only shows motional heterogeneity, further spin diffusion experiments are necessary to establish whether these segments are mixed homogeneously or not.

The rigid behaviour of the polyamide segments is consistent with complete phase separation, being as predicted from the homopolymer. However, the presence of a significant fraction of rigid polyether segments is at variance with the idea of a high degree of phase separation, unless the polyamide domains exert a strong constraint on the mobility of the polyether segments at the interface. Based on the homopolymer properties, the long T_2 exponential can only arise from the polyether segments.

A comparison of the ^{1}H FIDs of the control and irradiated P(EO,N12) samples shows that there is a reduction in the overall mobility of the polymer upon irradiation. This is shown by the increase in the fraction of the gaussian component and its decreasing T_2, as well as by the marked decrease in the fraction of the exponential components and in particular by the decrease in the T_2 of the long T_2 exponential component. These results are consistent with radiation damage causing cross-linking between the mobile polyether segments. A comparison of the two irradiated polymers shows clearly that repeating the radiation dose has no further effects on the polymer mobility. However, this does not rule out the possibility of further cross-linking because this may be taking place within the rigid segments where any additional cross-links would not be observable as the polymer is already in the rigid limit.

Analysis of ^{1}H T_1 and $T_{1\rho}$ relaxation times are complicated in phase separated polymers by the presence of spin diffusion [16]. A single common relaxation time will be seen when the separation of the phases, d, is of the order of [17]:

$$d = \sqrt{6D_s T_{1,1\rho}}$$

With a typical spin diffusion coefficient, D_s, of $4 \times 10^{-16}\ \mathrm{m^2\ s^{-1}}$ the single value of 0.39 s observed for the T_1 of the control implies a phase separation of much less than 20 nm, while the multi-component $T_{1\rho}$ suggest a domain size of greater than 2 nm. Complications in the analysis of $T_{1\rho}$ in the presence of spin diffusion mean that it is not possible to make unambiguous inferences about changes in the polymer dynamics or morphology despite the clear differences seen. When spin diffusion is present, multi-exponential fitting gives rise to a series of exponentials reflecting both the magnetisation transport and the inherent polymer dynamics [16]. It is then no longer possible to identify the various $T_{1\rho}$ components with unique phases. Thus, the observed decrease in the fraction of the long $T_{1\rho}$ component may represent a true increase in kHz motions or a decrease in the size of the less mobile domain, coupling it to a greater extent into the spin diffusion process and hence obscuring the inherent relaxation time to a greater extent. A possible increase in kHz motions is not necessarily inconsistent with more restricted motion on the T_2 timescale. For example, if the relaxation in the control is dominated by higher frequency motions restricting the motion will increase the spectral density at kHz frequencies.

Overall, the changes in the ^{1}H NMR relaxation times demonstrate a reduction in the polymer dynamics. Having observed these changes, the ^{13}C NMR spectra of the control and irradiated samples where examined to see whether significant changes were apparent in the chemical structure and phase composition. The ^{13}C CPMAS NMR spectrum of the control P(EO,N12), Fig. 2a, is remarkably similar to previously published data [5] on a polymer containing nearly five times as much polyether. Only small differences are seen in the relative intensities of the amide methylenes 44–20 ppm and the linewidth of the ether methylene at 71.4 ppm. The somewhat broader nature of the ether methylene is consistent with the ^{1}H T_2 results, in that it suggests the absence of mobility. Furthermore, the chemical shift is similar to the value reported for crystalline and amorphous PEO. Though given the short block length, it is unclear to what extent the chemical shift is a reliable reporter on the phase present. One explanation for the marked similarity in the spectra of the two polymers with radically different compositions is that the cross-polarisation conditions are in themselves selective for only the rigid components in the polymer. In both cases, the rigid phases have a similar composition because they represent the limiting mixing or interfacial polyether in the polyamide matrix. Additional polyether would then be present as a homopolymer type phase, which with its associated high mobility cross-polarises very poorly if at all. The differences in the ^{13}C CPMAS NMR spectra for the present samples and that previously reported indicate subtle changes in the chain packing and polymer dynamics, which may be attributable to the differences in polymer processing. Thus, whereas the previous data were on polymer analysed as received, in the present case, the polymer had been subjected to processing to make the balloon and stem. It is worthy of note that processing did not affect the polyamide phase present, the methylene adjacent to the nitrogen was observed to have a chemical shift of 40.2 ppm, corresponding to the γ-phase, as in the earlier report [5]. As noted above, although changes are seen in the relative intensities of the characteristic resonance of the polyamide and polyether segments in

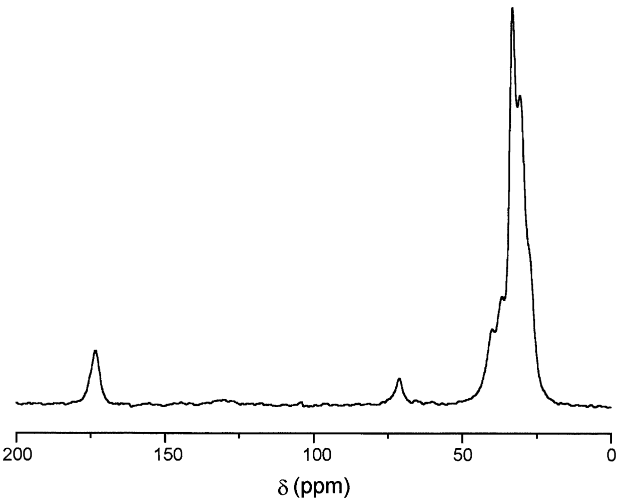

Fig. 3. ^{13}C CPMAS NMR spectra of the double dose irradiated poly(ether-*block*-amide). Normal CP, contact time 1 ms, recycle delay 3 s.

the selective ^{13}C NMR experiments, no experiment allowed the unique selection of one phase.

A close examination of the normal contact time ^{13}C CPMAS NMR spectrum for the control and irradiated polymer reveals a remarkable similarity, see Figs. 2a and 3. At best, only minor perturbations in the relative intensities in the amide and ether methylene resonance are seen. In addition, essentially no changes were seen in any chemical shifts. Similarly, the selective ^{13}C NMR spectra were to all intents and purposes identical. Thus, irradiation does not trigger profound changes in morphology unlike the case of PEO where crystallisation of the amorphous regions was seen. Rather the changes must be subtle, at the level of individual cross-link sites. These cannot be seen at the sensitivity of the current NMR experiments and would require the use of ^{13}C enrichment to be clearly identified.

4. Conclusions

Solid state NMR has been used to characterise the effect of electron beam irradiation on a poly(ether-*block*-amide) balloon used in angioplasty. The control processed polymer showed a complex ^{1}H FID reflecting a range of polymer dynamics. Selective ^{13}C NMR experiments were used to identify the rigid phase as containing both polyamide and polyether segments. On the basis of the ^{13}C chemical shifts the polyamide segments were found to adopt the γ-phase as is the case for homopolymer nylon-12. A mobile phase was present but could not be identified by a selective ^{13}C NMR experiment. Based on the homopolymer properties, it must arise from ether segments. ^{1}H T_1 and $T_{1\rho}$ suggests a domain structure on the 1–2 nm scale in the processed balloon. However, spin diffusion prevents the clear assignment of exponential fractions obtained in the fitting procedure to particular phases and thus quantification of the component phases. Irradiation leads to marked changes in the polymer dynamics as seen in the ^{1}H FID. In particular, there is an increase in gaussian content and shortening of the T_2 seen for the long T_2 exponential. Despite these changes, there is no clear evidence for a modification in the morphology, for example, there is no evidence for a new crystalline phase generated through the radiation damage. Any change associated with cross-linking or bond scission must be subtle at this level of irradiation. Doubling the dose of radiation does not cause further changes in the polymer dynamics, however, this does not exclude further chain events occurring in parts of the polymer already seen as rigid.

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