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Studies on irradiation stability of polystyrene by NMR

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Abstract The irradiation stability of polystyrene (PS) was studied by ^{13}C and ^{1}H NMR spectra, Nuclear Overhauser Relaxation (NOE) and ^{13}C NMR spin-lattice relaxation time (T_1). The results indicate that ^{13}C and ^{1}H NMR chemical shifts, NOE and T_1 were almost invariant with the increase of irradiation dose. This shows that polystyrene is particularly stable within 2.5 kGy doses and the mechanism of its stability is discussed.

Keywords Polystyrene, ^{13}C NMR, ^{1}H NMR, Irradiation stability
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1 Introduction

It is well known that NMR can be used to elucidate certain aspects of polymer structure and those properties, which are affected by molecular mobility.[1,2] In particular, the spin-lattice relaxation time (T_1) and Nuclear Overhauser Effect (NOE) are used to study properties of polymers and the manner in which these are modified by ionizing radiation.

2 Experimental

2.1 Materials and irradiation

Home-made linear polystyrene (PS) was irradiated by a ^{60}Co source of 3.7×10^{14} Bq at room temperature and a dose rate of 31.3 kGy/h with various total doses.

2.2 NMR measurements

^{13}C NMR spectra were recorded on Bruker AMX-500 spectrometer at 25 ℃ using $CHCl_3$ as solvent. Chemical shifts were measured with reference to the chemical shift of TMS as zero. The hydrogen resonance frequency was 500.13 MHz and the carbon resonance frequency was 125.75 MHz.

^{13}C NMR T_1 was measured by using $(180\text{-t-}90^{o})$ pulse sequence with recycle delay $>5T_1$ and error $<10\,\%$.

NOE was measured by the full and partial decoupled methods.

3 Results and discussion

There are no observable changes in ^{1}H and ^{13}C spectra of polystyrene after the irradiation of 2.5 kGy dose, which shows that the polystyrene is stable. This stability can be explained by the facts that a coordinate structure was formed by –CH- with the chain and its side group phenyl ring, which produced the free radical by the irradiation process. This stability of polystyrene is useful for preparing radiation-resistant materials or the graft copolymerization by radiation.

3.1 ^{1}H and ^{13}C NMR data for polystyrene

The ^{1}H and ^{13}C spectra of polystyrene consist of two peaks belonging to saturated carbon atoms, one of which is connected directly to the phenyl ring. Therefore, according to the chemical shifts of polystyrene, the ^{1}H and ^{13}C spectra of polystyrene were assigned preliminarily.

Table 1 shows that the chemical shifts of saturated carbon and hydrogen atoms of polystyrene are smaller than 46.0 (δ_C) and 2.0 (δ_H) respectively, but the chemical shifts of the phenyl ring carbon and hydrogen atoms of polystyrene are nearly at 6.46~7.04 (δ_H) and 1.43~1.84 (δ_H) respectively.

3.2 ^{13}C NMR spin –lattice relaxation time (T_1) of polystyrene

Since the ^{13}C NMR spin-lattice relaxation time

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(T_1) can provide detailed information on the overall molecular and segmental motion,[3,4] it can be used to characterize the structure and motion of polymer. The T_1 values of polystyrene before and after irradiation with different doses are given in Table 2.

Table 1 ^1H and ^{13}C NMR data for polystyrene

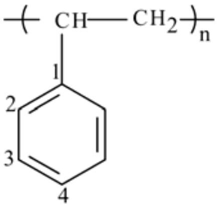
Structure	Position	δ_H	δ_C
	CH_2	1.43	45.80
	CH	1.84	40.32
	C^1	—	145.30
	C^2H	6.46	127.66
	C^3H	6.50	127.97
	C^4H	7.04	125.66

Table 2 ^{13}C NMR spin-lattice relaxation time (T_1) of polystyrene before and after irradiation with different doses

Dose (kGy)	Dose rate (kGy/h)	T_1 (ms)				
		C^1	C^2	C^3	C^4	CH
0	—	685.95	281.52	279.69	249.95	313.68
0.1	31.3	588.97	284.62	266.63	247.34	304.27
0.5	31.3	655.42	294.05	264.04	261.76	320.73
1.0	31.3	636.57	294.05	273.52	261.76	320.73
2.5	31.3	638.84	279.46	283.14	264.85	314.94

From Table 2 we can find that T_1 values of carbon are invariant before and after irradiation. This is attributed to the fact that the T_1 value of carbon atoms gives information mainly about high frequency and short range motion of the chain, and is insensitive to long range segmental motion in polymer structure. In addition, T_1 of C^1 before and after irradiation at room temperature is longer than that of phenyl ring. This retardation is caused by longer chain.

3.3 The NOE factor of polystyrene

The relationship between NOE and the irradiation dose is presented in Table 3.

Table 3 The NOE factor of polystyrene before and after irradiation with different doses

Dose (kGy)	Dose rate (kGy/h)	NOE				
		C^1	C^2	C^3	C^4	CH
0	—	0.06	0.44	0.44	0.38	0.48
0.1	31.3	0.05	0.40	0.49	0.41	0.69
0.5	31.3	0.06	0.48	0.49	0.41	0.61
1.0	31.3	0.12	0.44	0.49	0.50	0.62
2.5	31.3	0.02	0.49	0.49	0.48	0.69

As seen in Table 3, the NOE factors of C^1 in the phenyl ring and –CH- carbon in the main chains change more obviously than that of other carbons in the phenyl ring. In the organic systems, the NOE factor depends mainly on the relaxation mechanism and the molecular motion. When the relaxation mechanism is unchanged the NOE factor changes in the radiation system and depends mainly upon the effect of chain structure on segmental motion. Because the free radical of –CH carbon was produced by irradiation, the T_1 becames longer and the motion is slower. The free radical of –CH- with the phenyl for conjugate structure was ratifying again.

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