Chinese Chemical Letters Vol. 12, No. 4, pp. 353 – 354, 2001

Solid State NMR Study of Polystyrene Nanolatex Particles(I) ^{13}C Spin-Lattice Relaxation Time

Ya Lin TANG*, Xiao Zhong QU, Liu Sheng CHEN, Xi Gao JIN

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

Abstract: ^{13}C spin-lattice relaxtion times for polystyrene nanolatex particles have been investigated. It was found that the dramatic increase at 80℃ annealing temperature is well below the Tg temperature of bulk polystyrene, the increase of relaxation time of aromatic carbons is larger than that of for aliphatic carbons at transition annealing temperature.

Keywords: Polystyrene nanolatex particles, solid state NMR, spin-lattice relaxation time

A wide range of physical methods has been used for studying the sintering behavior of bulk polystyrene, which has been the subject of AFM imaging, DSC measurement, Dilatometer meadurement, Fourier IR, and solid state NMR studies to investigate the physicochemical change and its relation to the electronic and magnetic performance. In recent years, more attention was paid to the size effect on annealing temperature for the latex particles with the diameter of less than 100 nm, which present some novel condensed properties[1-3]. Liquid and solid state NMR spectroscopic studies have been undertaken on NMR measurement and some nanolatex particles[4-6]. However, there have been no NMR measurement and comparative study reported on the annealing temperature dependence of ^{13}C spin- lattice relaxation of polystrene nanolatex particles. In this paper we report the results of the ^{13}C spin-lattice relaxation time over a range of anealing temperature on polystyrene nanolatex particles samples.

^{13}C spin-lattice relaxation behavior has been measured for different annealing temperature samples by CPT_1 pulse sequence. The relaxation curves of individual carbon atoms of samples show a typical two-exponential characteristic. The values of long relaxation time T_{1L}, short relaxation time T_{1S},, and their contents P_L and P_S in both ploystyrene nanolatex particles obtained from ^{13}C spin-lattice relaxation curves are listed in **Table 1.**

Table 1 shows that C_4's T_{1L} in nanolatex sample has a transition at 80°C which is well below the glass-transition tempareture, Tg (*ca.*105°C), it was thought to be that the overlap of phenyl rings leads to higher increase of ^{13}C's T_{1L}. These experiment results are consistent with that AFM images and DSC measurements. AFM height images show that the particle boundary is clearly seen whenever the annealing temperature is below 80°C. The particle thermal behavior of nanolatex polystyrene particles, which was annealed for 1h at the different elected temperature below 95°C, was examined in

the DSC scan, an exothermic peak was found near Tg.

Table 1 ^{13}C spin-lattice relaxation time of aromatic and aliphatic Carbons in polystyrene nanolatex particles after annealing at different temperature for 1 hour

		25℃	80℃	90℃	100℃	110℃	120℃
C1	T_{1L}	93.26	103.79	108.54	108.33	113.54	110.79
	P_L(%)	71.87	78.21	79.65	78.91	80.49	79.47
	T_{1S}	6.75	7.26	7.59	7.81	8.03	7.97
	P_S(%)	28.13	22.79	20.35	21.09	19.51	20.53
C4	T_{1L}	90.47	101.78	112.87	119.87	118.95	118.73
	P_L(%)	69.78	76.64	80.24	81.14	80.75	80.67
	T_{1S}	4.94	5.56	5.78	6.24	6.35	6.31
	P_S(%)	30.22	23.36	19.76	18.86	19.25	19.33
Methylene	T_{1L}	92.49	99.88	104.54	106.77	108.81	108.47
	P_L(%)	81.74	86.59	88.09	89.04	89.87	89.56
	T_{1S}	7.54	8.07	8.39	8.45	8.47	8.81
	P_S(%)	18.26	13.41	11.91	10.96	10.13	10.44
Methine	T_{1L}	98.38	107.14	112.43	114.44	116.27	115.94
	P_L(%)	83.66	87.24	89.12	89.78	90.08	89.97
	T_{1S}	9.69	10.03	10.21	11.09	10.87	11.04
	P_S(%)	16.34	12.76	10.88	10.22	9.92	10.03

It was proposed that rotation of the phenyl rings may be hindered because of entanglement. **Table 1** shows that the increase of T_{1L} value of aromatic carbons is larger than that of T_{1L}'s for aliphatic carbons in nanolatex particles at 80°C annealing temperature. Compared to bulk particles[6], **Table 1** indicates that the T_{1L} values of aromatic carbons in nanolatex particles below 80°C are shorter than that in bulk polystyrene below Tg, while they become longer over 80°C than that in bulk particles polystyrene over Tg, it can be deduced that the phenyl rings in nanolatex particles are easier to overlap than in bulk polystyrene.

Acknowledgments

This work was supported by National Key Project for Fundamental Research (N.95-11) and National Natural Science Foundation of China (N.20004011 & 20023003).

References

1. A. Goudy, M. L. Gee, S. Biggs, *Langmuir*, **1995**, *11*, 4454.
2. S. Mazur, R. Bacherbaner, J. Buckholz, *Langmur*, **1997**, *13*, 4287.
3. A. G. Gillicinski , C. R. Hegedus, *Pro. Org. Coat*, **1997**, *32*, 81.
4. S. Jacob, M. D. Sefcik, E. O. Stejskal, R. A. McKay, *Macromolecules*, **1984**, *17*, 1107.
5. S. Z. Mao, G. L. Ding, H. Z. Yuan, *Science in China*, **1997**, *40*, 1.
6. S. J. Jia, L. S. Chen, X. G. Jin, *Science in China B*,**1998**,*28*,72.

Received 19 September, 2000