

**Abstract**  $^{13}\text{C}$  CP/MAS spectra and nuclear Overhauser effects (NOE) at room temperature have been measured for acrylonitrile (AN) in homophase irradiated polymerization. With the increase of radiation dose the chemical shift of cracking peaks and NOE are variation. This implies that the polymerized mechanism of AN were changed with the variation of irradiated doses and dose rate.

**Keywords:** Acrylonitrile    Irradiation    Polymerization

There is the stronger affinity electron group (-CN) in acrylonitrile monomer. It may be polymerized by various ways and mechanism and be gained the polymer of difference structures and molecular weight in polyacrylonitrile (PAN). Starmicarbon<sup>[1]</sup> and Starker<sup>[2]</sup> obtained higher molecular weight of polyacrylonitrile by peroxysulfate-pyrosulfite in oxidation-reduction system. The superhigh molecular weight of PAN was synthesized chemically according to the method of Wu et. al. <sup>[3]</sup> by suspension polymerization.

In this paper we discussed that the relative concentrations of steric dyads and triads in the chain structure in PAN and the irradiation polymerized mechanism of acrylonitrile monomer in room temperature by different dose and dose rate.

## 1 Experimental

### 1.1 The homophase polymerization of acrylonitrile

Acrylonitrile monomer were purified by decompression distillation and irradiated polymerization by  $^{60}\text{Co}$  source of  $3.7 \times 10^4$  Bq at room temperature. Irradiation doses of 50 and 100 kGy were used, and dose rate of 110 and 140 Gy/h were used.

### 1.2 $^{13}\text{C}$ CP/MAS spectra measurement

The high-resolution solid-state NMR spectra were obtained on a Bruker MSL-400 spectrometer. The resonance frequencies were 400.13 and 100.63 MHz for protons and  $^{13}\text{C}$  nuclei, respectively. The contact time of the cross-polarization was generally 1 ms. All the chemical shifts were referenced to  $\text{CH}_3$  peak of HMB. In order to suppress the side, the TOSS pulse train was used in CP/MAS experiment. Full nuclear overhauser effect (NOE) was measured by full and partial decoupled methods.

### 1.3 The measurement of viscosity

Ubbelodhe viscosimeter was used at  $26.0 \pm 0.1$  C and solvent is DMF.

## 2 Result and discussion

### 2.1 The relationship between chain structure and dosages

$^{13}\text{C}$  CP/MAS spectra of PAN and its assignment are shown respectively, in Fig.1 and Table 1 by acrylonitrile homophase polymerization and a dose rate of 110 kGy/h with various total doses.

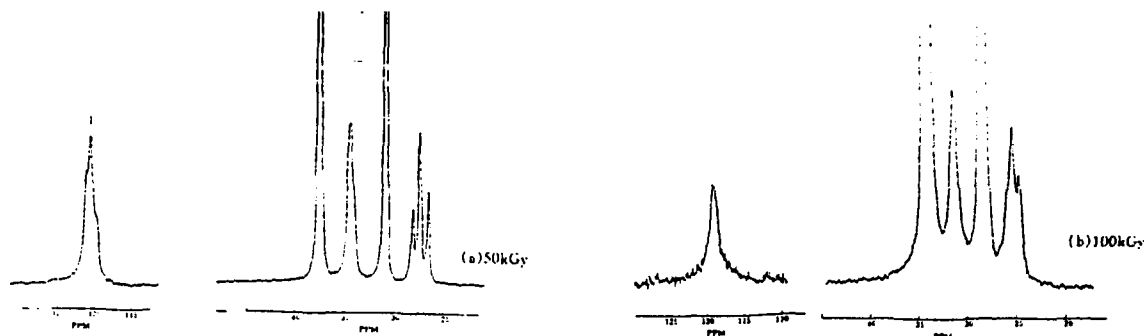


Fig.1 The  $^{13}\text{C}$  CP/MAS spectra of polyacrylonitrile at different doses

Table 1 gives the chemical shift of cracking carbon in PAN.

Table 1 the Chemical shift and relative area of polyacrylonitrile

Chemical group	Dose (kGy)			
	50		100	
	ppm	relative (%)	ppm	relative(%)
-CH	28.80	55.4	27.58	55.1
	27.27	100.0	26.93	100.0
	26.58	56.9	26.22	57.2
-CH <sub>2</sub>	32.85	39.7	33.95	38.2
	32.67	40.1	33.84	41.0
	32.47	15.1	32.53	16.2
-CN	119.65	16.9	119.48	18.2
	119.55	6.4	119.48	5.5
	119.24	8.2	118.20	7.8
	118.24	8.0	118.80	7.2

As seen in the Fig.1 and Table 1, There are three zones in  $^{13}\text{C}$  CP/MAS spectra from the lower to higher field it is  $-\text{CN}$ ,  $-\text{CH}_2$  and  $\text{CH}$  groups, respectively. The nitrile resonance of PAN appears at 120 ppm, the methylene carbon at 32.6 ppm and the methine carbon at 27.0 ppm. There are cracking peaks of every carbon in varying degrees, their chemical shift and relative area of peaks is shown in Table 1. From Fig.1 illustrates in  $^{13}\text{C}$  CP/MAS spectra of polyacrylonitrile we find that  $-\text{CH}$  and  $-\text{CH}_2$  group cracking four peaks. In former from the lower to higher field it homologous triads in steric configuration that is mm, mr and rr. In later from the higher to lower field, it homologous tetrads, there are mmm, mmmr, mmmr, mmmr and rrr six arrang. from every the line intensity and the peak area of spectra, we can obtain dispersity probability, then it was calculated by Bernoulli or first Markov model and decided polymerization mechanism.

For the radical polymerization of acrylonitrile, there are two termination ways that is two radicles and divergent termination, respectively, these terminated ways were produced possibility and results were raceme structure.

## 2.2 Influence of dose rate on the chain structure

Fig.2 (b) and (c) gives the  $^{13}\text{C}$  CP/MAS spectra of the nitrile carbon in acrylonitrile in homophase polymerization and a dose 100 kGy with various dose rates. Generally there is various actively center, in ethylene kind monomer by irradiation inducing e.g. radical, ionization matter and various excited states. therefore, there are correspondencely polymerization mechanism. Because there are stronger affinity electron group ( $-\text{CN}$ ) in structure acrylonitrile monomer it is easily polymerized by anion polymerization.

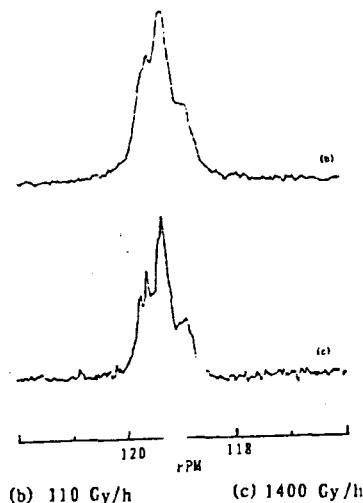


Fig.2 the  $^{13}\text{C}$  CP/MAS spectra of polyacrylonitrile at different doses rate

When dose and dose rate were the lower free radical and actively ion were produced simultaneously, but the polymerized rate of anion is the higher than free radical, thence in this condition anion polymerization occupied a dominant position.

As contrasted with the decrease of dose and dose rate in irradiation system the concentration of free radical were increased. In this time the collision possibility of the free radical was increased, that is, the addition low of monomer obeys Bernoullian process. The producing chain structure shows in Fig.2 (c). From these spectra it can be shown that PAN of irradiated polymerization is essentially a random polymer.

In addition, from molecular weight of polymer, with the increase of dose rate 0.11 to 1.4 kGy/h the decrease of viscosity from 2.22 to 0.10 dl/g. It indicated that the molecular weight of polymer was down repeatedly.

### 2.3 The effect of NOE factor

In the organic systems NOE factor depends mainly tow partes, that is, the contribution of relaxation mechanism and molecular motion<sup>[4]</sup>. The observed value of NOE at different irradiated doses are summarized in Table 2

Table 2 The NOE factor as a function of dose in polyacrylonitrile

Dose (kGy)	NOE		
	-CH	CH2	CN
50	1.98	2.04	1.26
100	2.18	2.06	1.19

As seen in Table 2, the value of NOE was changed in PAN at deffrent doses. When the relaxation mechanism is not changed in PAN, only the macrimoleculer chain motion causes The changing of value of NOE. The defferent chain motion represents different chain structures that it is decided polymerization mechanism.therefore the influnce of iiradiation doses on polymerization mechanism was testefied again.

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