

STUDY ON THE SYNTHESIS AND STRUCTURE OF MACRORETICULAR BEAD PAN/PVC IPN RESINS*

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ABSTRACT

Macroreticular bead PAN/PVC IPN resins with cyano and chloro groups were synthesized by interpenetrating polymerization of acrylonitrile, or acrylonitrile and divinylbenzene into a macroporous polyvinyl chloride bead. The composition and structure of the bead IPN resins have been investigated by means of FT-IR, NMR, SEM, mercury porosimetry and elemental analysis. During the process of interpenetrating polymerization, the chain propagation obeys Bernoullian statistical law, and no grafting polymerization has been observed. The content of cyano group in the resulting IPN resins can be adjusted by the amount of acrylonitrile added. The morphology of the IPN resins basically resembles that of the polyvinyl chloride bead, whereas the pore structures vary to a certain degree.

INTRODUCTION

Macroporous bead resins of chemically modified polyacrylonitrile (PAN) and polyvinyl chloride (PVC) have a wide variety of applications. They are known as exchangers, sorbents and carriers for biologically active substances and so forth¹⁻³. Considering that a macroreticular bead resin containing both cyano and chloro groups would offer interesting possibilities for further chemical modification, we undertook the synthesis of macroreticular bead PAN/PVC IPN resins (PAN/PVC MR-IPN resins) by interpenetrating polymerization of either acrylonitrile (AN) or AN and divinylbenzene (DVB) into a macroporous bead PVC matrix. The suspension polymerization process of AN in the presence of bead PVC, the chemical composition, structure and morphology, as well as the pore structure of the resulting PAN/PVC MR-IPN resins have been studied by means of FT-IR, NMR, SEM, mercury porosimetry and elemental analysis. Preliminary results show that the chain propagation of AN polymerization obeys Bernoullian statistical law and relative content of cyano and chloro groups in the MR-IPN resins can be adjusted by the amount of AN monomer added. No grafting reaction of AN onto PVC chain has been observed in the polymerization process. The morphology of the resulting MR-IPN resins basically resembles that of the bead PVC used, but the pore structures vary to a certain degree.

EXPERIMENTAL

Materials and instrumentation

Bead PVC, a linear polymer with macroporous structure (particle size: 0.3 ~ 1.3mm), provided by Yanguoxia Chemical Factory of Gansu Province AN(A R grade), purified by distillation (BP: $77 \pm 1^\circ\text{C}$ /760mmHg). DVB (A R grade, DVB content 45%), after

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adding 0.1% hydroquinone, distilled under reduced pressure (B. P. $42 \pm 1^\circ \text{C}$ /4mmHg).

Elemental analysis were carried out by using a Carlo Erba elemental analyzer model 1106 FT-IR spectra were recorded on a Nicolet FT-170 SX spectrophotometer. NMR spectra were determined on a Bruker AM-400 spectrometer at room temperature, using DMF- d_7 as solvent; Tetramethylsilane (TMS) in CCl_4 solution was taken as reference; The broadband decoupling (BB) and distortionless enhanced by polarization transfer (DEPT) techniques were employed in the determination. SEM photographs were obtained on a Hitachi $\times 650$ scanning electron microscope. The pore parameters were measured by a Carlo Erba 200 mercury porosimeter.

IPN resin synthesis

15g bead PVC was placed into a 500ml three-necked flask fitted with stirrer, reflux condenser and thermometer, then a given amount of AN containing 1% BPO, or a cyclohexanone solution of AN and DVB containing 1% BPO was added. The mixture kept at room temperature for 2hr. With stirring, 2 ~ 3g calcium carbonate, and a solution made up of 10 ~ 15ml of 2% gelatine water solution and 20 ~ 30g anhydrous sodium sulphate in 200 ~ 250ml deionized water were added into the flask successively. The suspension polymerization was carried out at 65°C for 2hr; 75°C for 2hr; 85°C for 1.5hr and 90°C for 1hr by using a water-bath. The resin was cooled and filtered, washing with hot water, 95% ethanol, 1M HCl, and again with water until chloride-free. The resin was dried, extracted with acetone in a Soxhlet extractor for 48 hr, and then dried again under vacuum.

RESULTS AND DISCUSSION

Chemical composition and structure

In Table 1, the relative content of PAN% and PVC% in the resins was calculated from the elemental analysis data of N% and Cl% found. It demonstrated that PAN% increases with the increasing of the amount of AN monomer added. For resin D, E and F, it seems that the crosslinking agent DVB would be favourable for the interpenetrating polymerization of AN into the bead PVC matrix.

Table 1 Experimental data of PAN/PVC MR-IPN resins

Resin No	A	B	C	D	E	F
AN: PVC (w/w)	1	1.5	2	1	1.5	2
PVC: CyH* (w/w)	0	0	0	3	3	3
CD** for PAN (%)	0	0	0	2.5	2.5	2.5
N% (found)	7.9	12.2	16.5	12.3	14.4	15.8
Cl% (found)	37.2	30.3	20.7	27.4	20.7	15.9
PAN%	29.9	46.6	62.5	46.6	54.6	59.9
PVC %	65.8	53.6	36.6	48.5	36.6	28.1

* Cyclohexanone; ** Crosslinking degree

Fig 1 illustrates the FT-IR spectra of PAN/PVC MR-IPN resin C and F. The FT-IR spectra show that the resins contain both cyano ($\nu_{\text{C}=\text{N}}$, 2244cm^{-1}) and chloro ($\nu_{\text{C-Cl}}$, 711, 614 and 533cm^{-1}) groups. The FT-IR spectra also show characteristic absorption at 835 and 802cm^{-1} due to the vibrations of para- and meta-phenylene group in the resin F respectively. $^1\text{H-NMR}$ spectrum of the resin C (Fig 2) shows the resonance bands of methylenic protons for both PAN and PVC overlapped in a broad singlet (2.0 ~ 2.6 ppm), and methinic protons for PAN (3.3 ppm). While those of methinic

protons for PVC are at 3.5 and 4.4 ppm, this is due to the influence of interpenetrating PAN on the chemical shift. On the other hand, there appears a resonance peak of amide protons at 4.5—4.7 ppm. Correspondingly, FT-IR spectra (Fig. 1) also indicate characteristic absorption of amide group (ν_{N-H} 3536 cm^{-1} ; $\nu_{C=O}$ 1634 cm^{-1}). This should be resulted from the hydrolysis of a few cyano groups in the MR-IPN resins.

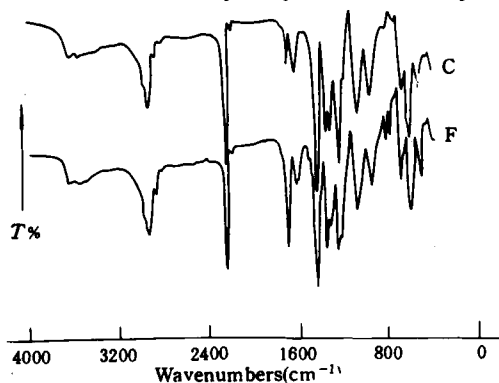


Fig. 1 FT-IR spectra of PAN/PVC MR-IPN resins (C-resin C; F-resin F)

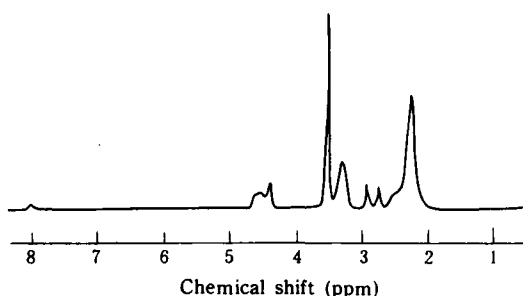


Fig. 2 ^1H -NMR spectrum of the resin C

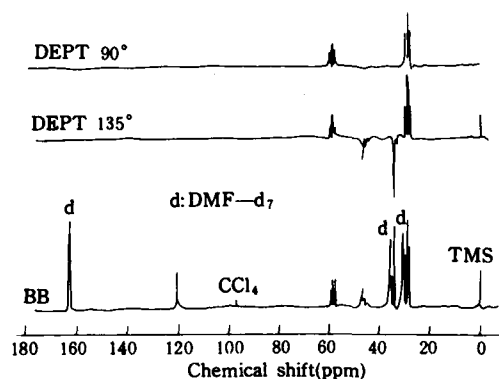


Fig. 3 ^{13}C -NMR spectra of the resin C

Polymerization process and microtacticity

^{13}C -NMR spectra of the resin C are illustrated in Fig. 3. The BB, DEPT 135° and 90° spectra show that there is no resonance peak at 70 ~ 80 ppm. The absence of a peak at δ 70 ~ 80 ppm corresponding to a grafting carbon^[8] may be considered as that there must not have grafting reaction taken place in the course of the interpenetrating polymerization. Fig. 3 also shows the presence of carbon resonance bands at 45 ~ 47 ppm (methylene) and 57 ~ 59 ppm (methine) for PVC; meanwhile, 34 ppm (methylene), 27 ~ 29 ppm (methine) and 120 ppm (cyano group) for PAN.

The microtacticity and corresponding chemical shift of the resin C are listed in Table 2. The resonance band for cyano carbon shows a sextuplet (tetrad) but is not a decuplet (pentrad)^[8, 10]. This phenomenon probably is due to the influence of the bead PVC on the microtacticity of the interpenetrating PAN.

Fig. 3 also exhibits that the relative intensities of the triplet of methinic carbon for PAN have the following relation:

$$\text{mm} : \text{mr} : \text{rr} = 0.28 : 0.48 : 0.24$$

Concerning the PAN/PVC MR-IPN resins obtained, resin D, E and F are designated as a semi-IPN of the second kind (semi-2), because polyvinyl chloride is not crosslinked but polyacrylonitrile is crosslinked^[9]. Although polyvinyl chloride and polyacrylonitrile are not crosslinked in the resin A, B and C, the chain entanglement between PVC and PAN was formed by interpenetrating polymerization of AN into the bead PVC, and the non-bond network is similar to a thermoplastic IPN^[7]. Thus, resin A, B and C can be regarded as a pseudo-IPN.

Table 2 Microtacticity and chemical shift of the resin C *

PVC				PAN					
CH		CH ₂		CH ₂		CH		CN	
Conf **	ppm	Conf	ppm	Conf	ppm	Conf	ppm	Conf	ppm
mm	57.24	mmm	44.90	mm	33.85	mm	27.63	mmm	121.20
mr	58.13	mmr	45.50	mr	34.02	mr	28.51	mmr	121.00
rr	59.11	mmr	45.85	rr	34.22	rr	29.08	mmm	120.75
		mrr	46.51					mrr	120.42
		mmr	46.85					mrr	120.07
		rrr	47.01					rrr	120.00

* m , meso (or isotactic) ; r , racemic (or syndiotactic) .
** conf . , configuration

The above ratio agrees with Bernoullian statistics⁽¹¹⁾ well. In other words, the chain propagation of AN polymerization obeys Bernoullian statistical law in the interpenetrating polymerization of AN, while the structure and microtacticity of the bead PVC did not exert marked influence on the random propagation of AN monomer.

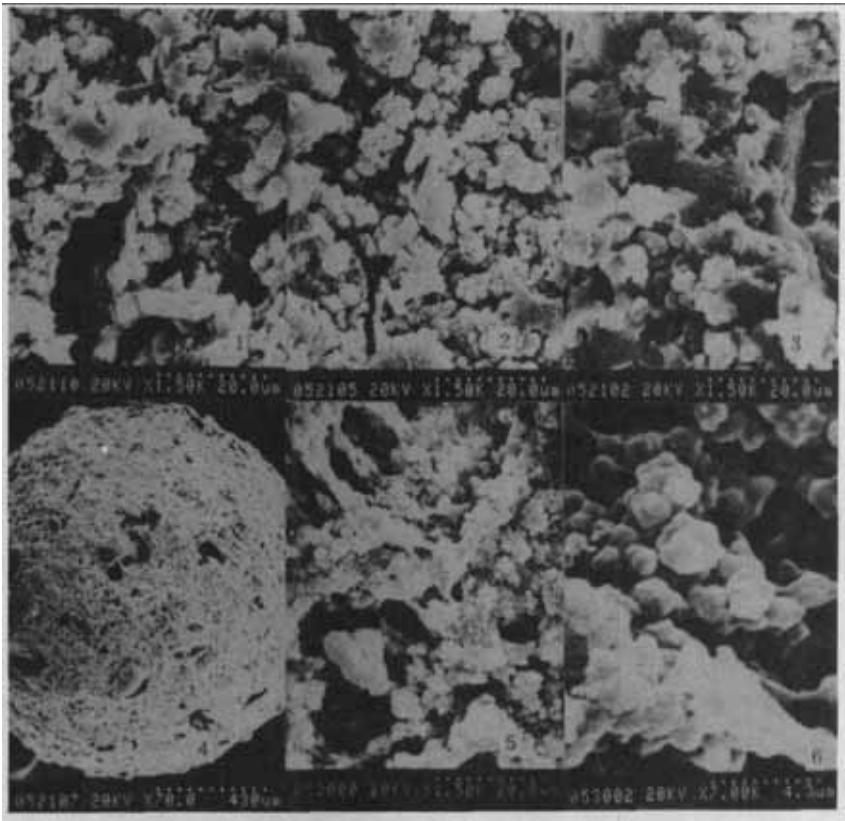


Fig. 4 SEM photographs of several bead resins

- Note: I, The photograph 1, 2 and 3 show section photographs enlarged to 1500 times (1, bead PVC; 2, resin C; 3, resin F)
II, The photograph 4, 5 and 6 are surface photographs of resin C, and enlarged to 70 , 1500 and 7000 times successively.

The morphological structure

Fig 4 shows a set of SEM photographs of the bead PVC and PAN/PVC MR-IPN resins. In comparison with the bead PVC, the SEM photographs of PAN/PVC resins exhibit that there still exist both agglomerates of minutely spherical gel particles and superlarge pore-holes, resembling the bead PVC. This indicates that the interpenetrating polymerization of AN did not change the morphology of the bead PVC. Meanwhile, no obvious phase separation was observed in the SEM photographs of PAN/PVC resins. It also reflects that the compatibility between PAN and PVC is well enough.

The pore structure and distribution

The pore structure parameters of the bead PVC and PAN/PVC MR-IPN resins have been investigated by mercury porosimetry, and the data obtained are listed in Table 3. As a result of interpenetrating polymerization, the most probable distribution of pore radius, specific surface area and pore volume as well as average porosity of the resin C are less than those of the bead PVC matrix, but the average pore radius has become much larger. As to the resin F, except the pore volume and average porosity, other pore structure parameters are larger than those of the bead PVC. In the former case, it may be due to the swelling and interpenetrating polymerization of AN monomer into the bead PVC in the polymerization process. The change of pore structure parameters in the latter case is mainly due to both pore-creating and swelling of the cyclohexanone used.

Table 3 The pore parameters measured by mercury porosimetry

Resin No	PVC	C	F
Specific surface area (m ² /g)	1.30	0.64	2.49
Specific pore volume (cm ³ /g)	0.454	0.185	0.385
The most probable distribution of pore radius (Å)	6200	4130	7520
Average pore radius (Å)	7060	11150	11330
Average porosity (%)*	40.28	36.84	28.37

* The data provided by SEM statistical analysis^{1,2}

The pore distributions of the resin C and F are illustrated in Fig 5 and 6. The $dv/dr - \ln r$ curve shows that the pore radii of the resin C are distributed in macroporous domain from 1097 Å to 22026 Å. In reference to the resin F, it exhibits a wide range of pore distributions from 55 Å to 59874 Å. These data are in good

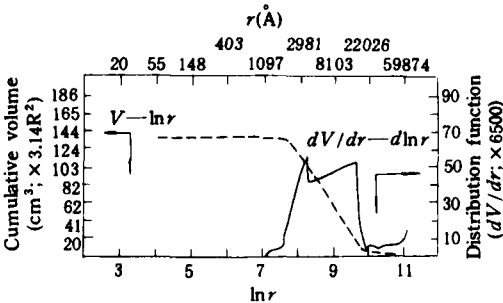


Fig. 5 The curves of mercury porosimetry on the resin C (R, the tube radius of mercury porosimeter)

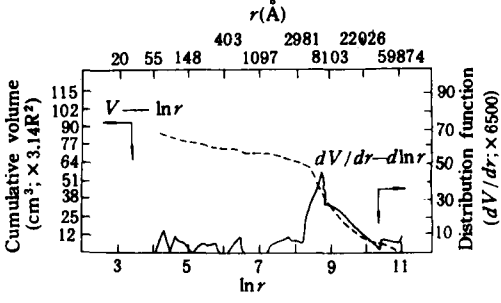


Fig. 6 The curves of mercury porosimetry on the resin F (R, the tube radius of mercury porosimeter)

agreement with the data listed in Table 3. In addition, the difference of the pore distribution between the resin C and F are shown by the data listed in Table 4.

Table 4 Percentage of different size pore in total pore volume (%)

Resin No	Total pore volume (cm ³ /g)	The domain of pore radii (Å × 10 ⁻³)						
		0.25	0.25—0.5	0.5—1.0	1.0—1.5	2—5	5—10	10—75
C	0.185	0.00	0.00	0.00	0.34	30.84	29.83	37.82
F	0.385	10.83	2.73	3.67	0.06	13.38	34.02	33.05

Keywords:

IPN synthesis; PAN/PVC Macroreticular—resin; Bead PVC; Structures; Interpenetrating Polymerization

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