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Xiaoning Liu^a; Jinglu Chen^b; Rongqing Wei^a; Gi Xue^b

^a Department of Biochemistry, Nanjing University of Chemical Technology, Nanjing, P.R.China

^b Department of Polymer Science & Engineering, Nanjing University, Nanjing, P.R.China

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**INFRARED SPECTRA INVESTIGATION ON PENDENT
DOUBLE BONDS IN MONODISPERSE MICRON
MACROPOROUS RESIN**

KEY WORDS: Macroporous resin, IR spectra, Pendent double bonds

Xiaoning Liu¹, Jinglu Chen², Rongqing Wei¹ and Gi Xue^{2*}

¹*Department of Biochemistry, Nanjing University of Chemical Technology, Nanjing 210009, P.R. China*

²*Department of Polymer Science & Engineering, Nanjing University, Nanjing 210093, P.R. China*

ABSTRACT

Monodisperse micron macroporous polystyrene resins were synthesized with different crosslinking degrees. The IR ratio of $A_{980\text{cm}^{-1}} / A_{790\text{cm}^{-1}}$ was selected to make the working curve and then determine the amount of pendent double bonds in resin. The result was compared with that of Bartholin's measurement. A Standard working curve method is very convenient, especially in the measurement of moderate and highly crosslinked macroporous resin, it's more accurate.

* Corresponding author.

INTRODUCTION

Monodisperse micron macroporous resin is widely used as a chromatographic fractionation column filler, a solid state synthesis carrier, and a catalyst carrier because of its uniform bead radius distribution and large specific surface area.

During preparation of macroporous resins with different rigidity, we have found that the crosslinked macroporous resin contains some unreacted residual double bonds (pendent double bond). The amount of these pendent double bonds increases with the amount of crosslinking agent used during the synthesis process. The unreacted pendent double bond can be used to prepare grafted copolymers for resin modification. This copolymer is used as polymer supports in solid state catalyst and enzyme fixation¹⁻⁵. So the measurement of the amount of pendent double bonds is important in the postfunctionalization of this resin.

EXPERIMENTAL

Monodisperse Polystyrene (PS) seeds were prepared by suspension polymerization¹. The PS seeds were swollen in the emulsion containing styrene, divinylbenzene, emulsifying agent, initiator and water, and then polymerized for 24 hours at 90°C in an oil bath. According to the amount of divinylbenzene used, the PS microspheres with different crosslinking degrees were obtained. The diameter of the microsphere is about 6 microns, measured from a transmission electron microscope (TEM).

Infrared spectra of macroporous resin were recorded from KBr-pellets (1wt.-% of polymer) in a Bruker IFS 48 FT-IR spectrometer. A Bruker MSL 200 NMR spectrometer was used to measure the solid state NMR spectra of these samples.

RESULTS AND DISCUSSION

As macroporous resin is a crosslinked polymer, which can't be dissolved in solvent or molten, it's difficult to measure the amount of pendent double bonds, especially in chemical methods. Solid state NMR measurement can obtain some useful results, but it's difficult to measure quantitatively. The amount of the pendent double bonds increases with the amount of crosslinking agent used during the synthesis process. This can be demonstrated from solid state NMR and IR spectra. FIG. 1 and FIG 2 show the ^{13}C -CP/MAS NMR and IR spectra of monodisperse macroporous resin with different crosslinking degrees, respectively.

Bartholin⁶ reported the measurement of the amount of pendent double bonds in IR spectroscopy. In his experiment, the absorption bands at 1610cm^{-1} and 980cm^{-1} were chosen as the characteristic absorption of double bonds, 780cm^{-1} and 1495cm^{-1} bands as the characteristic absorption of *meta*-disubstituted phenyl ring and *para*-disubstituted phenyl ring, 1470cm^{-1} and 748cm^{-1} as the characteristic absorption of monosubstituted phenyl ring. The results from Bartholin's method are listed in Table1.

In Bartholin's method, there were too many characteristic absorption bands that affected each other in a complex manner, and the baseline was also difficult to choose. In this paper, divinylbenzene (DVB) and diethylbenzene (DEB) were used as model compounds to obtain the standard curve. The measured data and resultant curve are shown in Table 2 and FIG. 3, respectively. Then the IR spectra of unknown macroporous resins are measured and the absorption intensity ratios of 980cm^{-1} / 780cm^{-1} are obtained, the corresponding amount of pendent double bonds are read

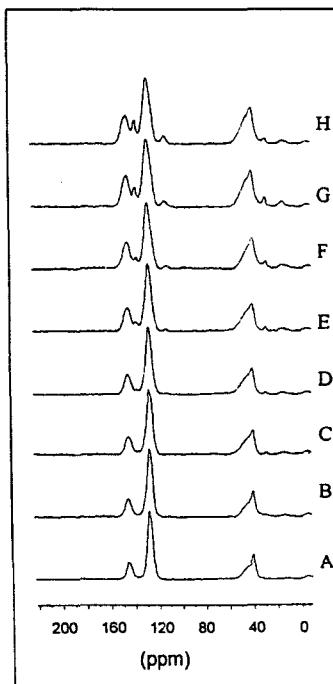


FIG.1. ^{13}C -CP/MAS NMR spectra of monodispersed macroporous resins with different crosslinking degree. A, 1%; B, 10%; C, 20%; D, 30%; E, 40%; F, 50%; G, 65%; H, 80%.

from the standard curve. FIG. 3 shows the measured results. The obtained amount of pendent double bonds is also listed in Table 1 as to compare with the results from Bartholin's method.

Comparing the results of the two methods, we can conclude that:

Firstly, for the moderate crosslinked macroporous resin, the results from two methods are in good agreement (with an error of 1%).

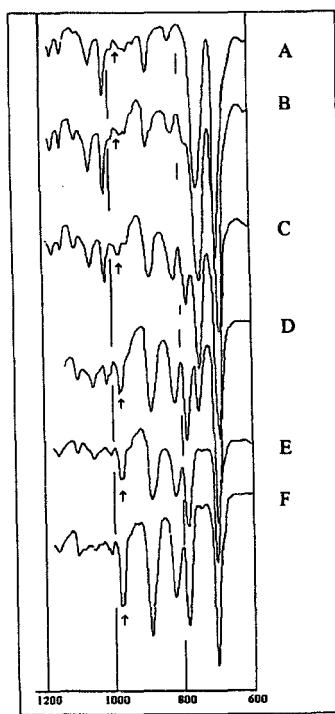


FIG. 2. IR spectra of monodispersed macroporous resins with different crosslinking degree. A, 1%; B, 10%; C, 30%; D, 50%; E, 65%; F, 80%.

TABLE 1. Results of the Amount of Pendent Double Bonds Obtained from Two Methods

Sample No.	Crosslinking degree (%)	$A_{980\text{cm}^{-1}}/A_{790\text{cm}^{-1}}$	Amount of double bonds (mmol/g)	
			Working curve	Bartholin's method
1	10	0.23	0.39	0.12
2	30	0.29	0.57	0.41
3	50	0.5	1.1	1.12
4	65	0.57	1.31	1.59
5	80	0.62	1.48	1.82

TABLE 2.
Composition of Making Working Curve and IR Results

DEB(ml)	5	5	5	5	5	5	5	5	0
DVB(μ l) ¹	0	20	50	100	200	500	1000	1200	5000
$C_{C=C}^{*2}$ (mmol/g)	0	0.06	0.15	0.30	0.59	1.40	2.56	2.98	15.4
$A_{980\text{cm}^{-1}}/A_{790\text{cm}^{-1}}$	—	0.07	0.11	0.19	0.31	0.62	0.90	1.02	—

*¹: commercial grade DVB (containing 80% DVB)

*²: calculated theoretical amount of double bonds

$$C_{C=C} = 2 * 1000 * V_{DVB} / ((V_{DVB} + V_{DEB}) * M) = 15.38 V_{DVB} / ((V_{DVB} + V_{DEB})$$

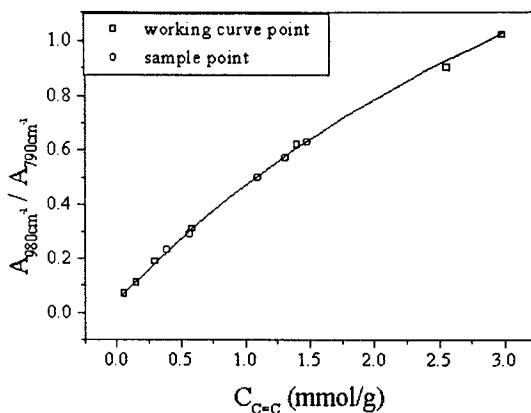


FIG. 3. Working curve obtained from IR ratio of $980\text{cm}^{-1}/790\text{cm}^{-1}$.

Secondly, for the highly crosslinked macroporous resin, the result from Bartholin's method is 23% larger than that from the standard curve method. It can be ascribed to the absorption of monosubstituted phenyl ring chosen as the characteristic absorption bands in Bartholin's method. In the measured samples, monosubstituted phenyl rings have not existed in the highly crosslinked samples (e.g. 65% or 80%), only disubstituted phenyl rings. As an example, the 65% crosslinking monomer contains 65% disubstituted divinylbenzene and 35% disubstituted vinyl ethlybenzene. In the calculation of the amount of double bonds, Bartholin's method overestimated the influences of the monosubstituted group, which led to the overhigh results. From this point, in the measurement of the amount of pendent double bonds in highly crosslinked macroporous resin, the standard curve method is more accurate than Bartholin's method.

Thirdly, contrary to the above condition, for the slightly crosslinked macroporous resin, the result from Bartholin's method is only 30% of that from the standard curve method. The reason is that the model monomers used in the standard curve are all disubstituted benzene (DVB and DEB) and don't contain monosubstituted benzene, but the actual measured sample contains monosubstituted benzene (styrene). This condition is more consistent with the consideration of Bartholin's method. So Bartholin's method is more reliable in the measurement of the amount of pendent double bonds in slightly crosslinked macroporous resin.

CONCLUSION

In the measurement of the amount of pendent double bonds in highly crosslinked macroporous resin, Bartholin's method is inconvenient in use and its calculation is

complicated. For highly crosslinked macroporous resin, this method has some defects in theory. Compared with Bartholin's method, the standard curve method is very convenient, especially in the measurement of moderate and highly crosslinked macroporous resin, it is more accurate.

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