

Supplementary information

S1. The chemical materials

N-vinylformamide (NVF) from Aldrich Inc. was distilled under vacuum and stored at -15°C . 2, 2'-Azobis (2-methylpropion-amidine) dihydrochloride (AIBA) from Aldrich Inc. was recrystallized from ethanol and stored at -15°C . 201 \times 7 strongly basic anion exchange resin was purchased from Chemical Plant of Nankai University (China) and regenerated before use. Ethanol and hydrochloric acid were of analytical grade and used as received. PVAm was obtained according to a method in the reference ¹. EDA, PIP, MEA and MC (99.0% purity) were obtained from Aladdin Reagent Co., Ltd. and used without further purification.

S2. The intermolecular hydrogen bonds in the SMA modified PVAm

The possible intermolecular action between SMA and PVAm was investigated by ATR-FTIR and the spectra are displayed in Fig. S1. It was found that the sharp characteristic bands around 3284 and 3368 cm^{-1} , which represent the free primary amine group of EDA ², do not appear. Compared with the pure PVAm, the intensity of absorption band of the EDA modified PVAm around 1660 cm^{-1} , which is assigned to the C=O stretching vibration (Amide I) ³, decreased obviously, meanwhile the intensity of absorption band around 1156 cm^{-1} , which can be assigned to the C-O stretching vibration ⁴, increased apparently. The result suggests that the intermolecular hydrogen bonds formed between oxygen atom of amide group in PVAm and primary amine group of EDA. Moreover, compared with the pure PVAm, the NH stretching vibration band (3180~3370 cm^{-1}) of primary amine group in the EDA modified PVAm shows broadening. This suggested that the intermolecular hydrogen bond can also

form between the lone pair on the very electronegative nitrogen atom of primary amine group in PVAm and the slightly positive hydrogen atom of primary amine group in EDA⁵.

Compared with the pure PVAm, the intensity of adsorption band of the PIP cross-linked PVAm around 996cm^{-1} assigned to the C-N stretching vibration, a characteristic band of PIP^{6,7}, increases obviously, and the sharp characteristic band around $3200\sim 3300\text{cm}^{-1}$ which represents the secondary amine group of PIP⁸ does not appear. The above results show that there is no free PIP in the PIP modified PVAm. Therefore, it can be deduced that hydrogen bonds form between PIP and PVAm. Moreover, the lone pairs on the very electronegative oxygen atom of amide group or nitrogen atom of primary amine group in PVAm have strong intermolecular action with the slightly positive hydrogen atom of secondary amine group of PIP⁵. The intensity of absorption band around 1660cm^{-1} which is assigned to the C=O stretching vibration (Amide I)⁴ has no obvious changes. The result indicates that the hydrogen bonds cannot form between the secondary amine group of PIP and the amide group in PVAm. According to the above analysis, it can be concluded that the intermolecular hydrogen bonds in the PIP modified PVAm formed between the secondary amine group of PIP and the primary amine group in PVAm.

As shown in Fig. S1, there is no free primary amine group in the MEA modified PVAm⁴. The stretching vibration absorption band of the free hydroxyl is $3500\text{-}3700\text{cm}^{-1}$, and when the intermolecular hydrogen bonds formed, the stretching vibration absorption band of the hydroxyl is in the range of $3200\text{-}3450\text{cm}^{-1}$ ⁴. According to Fig.

S1, there is no free hydroxyl in the MEA modified PVAm. Since there is no reaction between the MEA and PVAm⁵, it can be deduced that the hydrogen bonds formed between the MEA and PVAm. The C=O stretching vibration adsorption band around 1600 cm⁻¹ of amide group⁹ in the MEA modified PVAm is almost the same with that in the pure PVAm, which indicates that the intermolecular hydrogen bonds cannot form between the hydroxyl and primary amine groups of MEA and the amide group in PVAm. Moreover, the lone pairs on the very electronegative oxygen atom of hydroxyl group or nitrogen atom of primary amine group in MEA have strong intermolecular action with the slightly positive hydrogen atom of primary amine group in PVAm⁵. Therefore, the intermolecular hydrogen bonds in the MEA modified PVAm formed between the hydroxyl and primary amine groups of MEA and primary amine groups in PVAm.

According to Fig. S1, there is no free primary amine group in the MC modified PVAm¹⁰. The stretching vibration absorption band of the free ester group is 1070-1080 cm⁻¹, and when the intermolecular hydrogen bonds formed, the stretching vibration absorption band of the ester group is 1050 cm⁻¹¹⁰. As shown in Fig. S1, there is no free ester group in the MC modified PVAm. Because there is no reaction between the MC and PVAm⁵, it can be deduced that hydrogen bonds form between MC and PVAm. Compared with the pure PVAm, the C=O stretching vibration adsorption band around 1600 cm⁻¹ of amide group⁴ of PVAm in the MC modified PVAm has no obvious change. The results indicate that the intermolecular hydrogen bonds cannot form between the ester or primary amine groups of the MC and the

amide group in PVAm. Therefore, the intermolecular hydrogen bonds formed between the ester or primary amine groups of the MC and the primary amine groups in PVAm.

S3. The treatment of the SMA modified PVAm samples for investigating the mass stability of the samples

For investigating the mass stability of the SAM modified PVAm, the SMA modified PVAm sample was treated as follows: as shown in Fig. S2, the pure Ar gas was saturated with water vapor by bubbling through a humidifier which was kept at 55°C and then passing through a dehumidifier to remove the condensate water. The different SMA modified PVAm sample (effective sample area=19.26cm²) was mounted in a circular stainless steel cell. The dehumidifier and the circular stainless steel cell were put in a constant temperature drying oven (CTJZH, DH201) and kept at 50°C. The pure Ar gas permeated through the sample, and the permeated gas was evacuated into the air. The feed pressure was increased to 2, 6, 11 and 21bar, respectively. After 4 hours, the feed pressure was reduced to 1bar and the mass of the sample was tested.

Literatures

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Figure caption

Fig. S1. ATR-FTIR spectra of the pure PVAm and the SMA modified PVAm

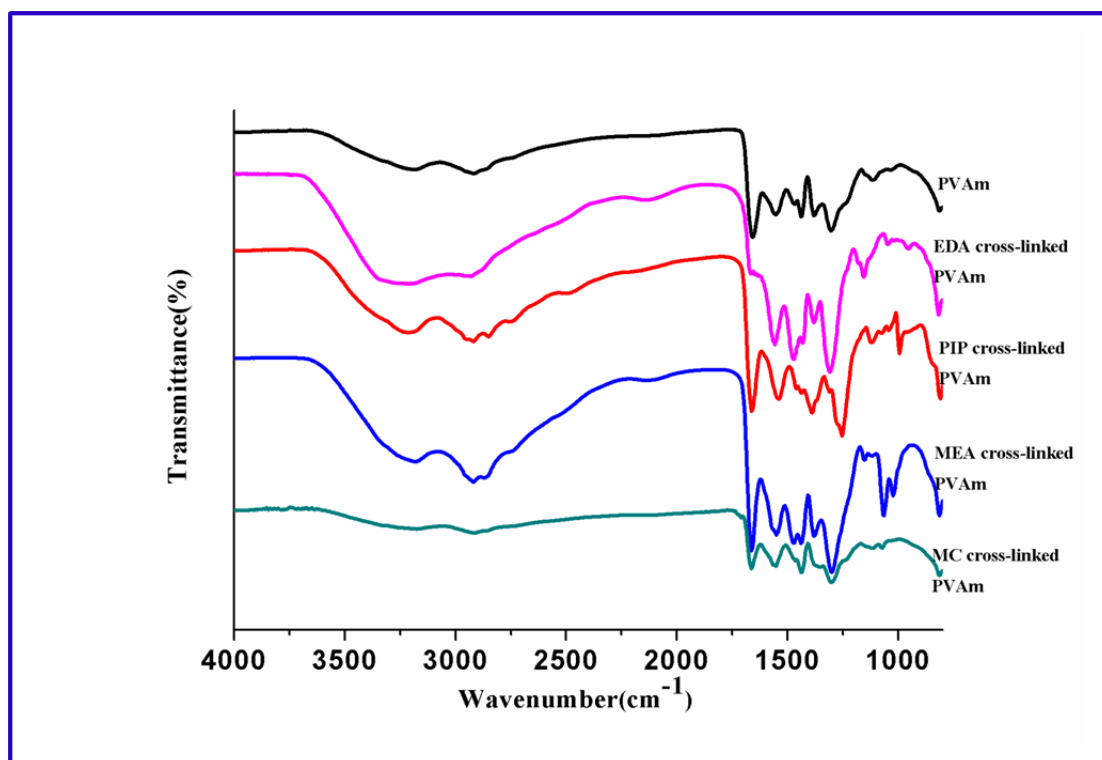


Fig. S1 ATR-FTIR spectra of the pure PVAm and the SMA modified PVAm

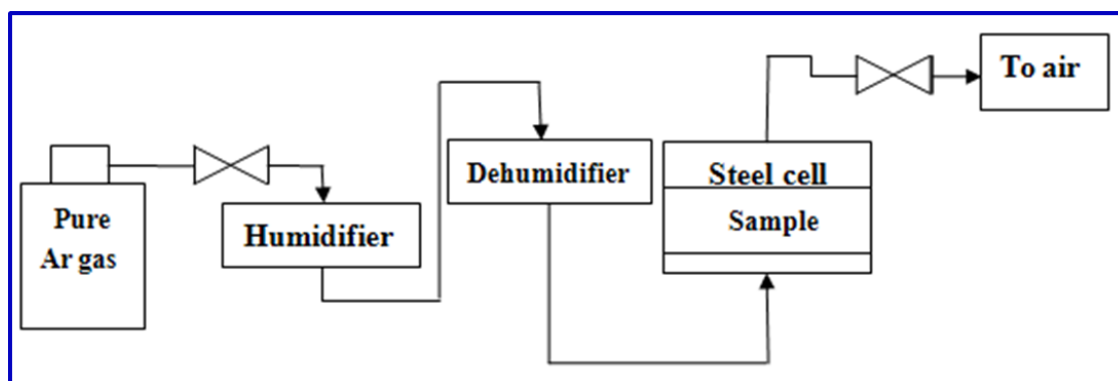


Fig. S2 Schematic drawings depicting the apparatus for investigating the mass stability of the SMA modified PVAm samples.