Synthesis of Highly Cross linked PMMA Nanoparticles and Their Application in Membrane and Opal Film

تحضير جسيمات النانونية لمتعدد البولي ميثيل ميثاكريلات النانوية عالية الترابط وتطبيقاتها في الغشاء النافذ ورقيقة العقيق

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Abstract :

In this study, we report a new method for the synthesis of highly crosslinked PMMA nanoparticles and their application in membrane and opal film fabrication . Cross linked PMMA nanoparticles were synthesized by using DVB as cross linker at 100 ^{0}C by soap-free emulsion polymerization . Membrane and opal film were synthesized from free PMMA nanoparticles and cross linked PMMA nanoparticles in different organic solvents. Free PMMA and cross linked PMMA nanoparticles treatment with toluene gave opal film and membrane structure meanwhile treatment with THF showed only membrane structure . The characterization of PMMA nanoparticles and their crosslinked ,membrane and opal film were done by FSEM , TEM and U.V.

Keywords: PMMA Nanoparticle, PMMA Cross Linked , Membrane and Opal Film .

الملخص :

في هذه الدراسة تقرير عن طريقة جديدة لتحضير جسيمات النانونية لمتعدد البولي ميثيل ميثاكريلات النانوية عالية الترابط وتطبيقها في الغشاء النافذ ورقيقة العقيق .

الترابط لمتعدد البولي ميثيل ميثاكريلات النانوية وتحضيره بواسطة استخدام ثنائي الفينيل البنزين كرابط عند درجة حرارة ١٠٠م ْ بواسطة بلمرة المستحلب الصابوني الحرة.

الغشاء النافذ ورقيقة العقيق تحضيره من جسيمات النانونية الحرة لمتعدد البولي ميثيل ميثاكريلات النانوية والتشابك النانونية جسيمات لمتعدد بولي ميثيل ميثاكريلات النانوية في اختلاف المذيبات العضوية .

متعدد بولي ميثيل ميثاكريلات الحرة والنشاط والترابط بجسيمات النانوية لمتعدد بولي ميثيل ميثاكريلات لمعالجته مع الطولوين يعطي رقيقة العقيق والتركيب الغشائي، بينما المعالجة مع رباعي هيدروفيرون يعطي فقط تركيب الغشائي النافذ .

والتحاليل التي أجريت لجسيمات لمتعدد ميثيل ميثاكريلات النانوية والترابط الغشائي ورقيقة العقيق درست بواسطة أجهزة الأشعة فوق البنفسجية (U.V) وXRD ,TEM .

الكلمات الرئيسة : جسيمات النانونية لمتعدد البولي ميثيل ميثاكريلات النانوية عالية الترابط، وتطبيقاتها في الغشاء النافذ ورقيقة العقيق .

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Introduction :

Highly Crosslinked PMMA nanoparticles , their membrane and opal films are used in a wide variety of scientific and technological applications with high-value-added materials, such as ion-exchangers, medical and chemical application as absorbents and polymer-supported catalyst[1−3]. Especially, there are strong demands for highly crosslinked polymer beads with superior heat and solvent resistance, mechanical strength to serve as a spacer for display panel, slip property improvement for plastic film and conductive balls[4−5]. The recent typical technique, which was used in the preparation of

monodispersed beads with micrometer diameter, is a dispersion polymerization [6−10]. This process is very attractive for large-scale preparation of such particles. Recently, the dispersion polymerization was studied to overcome the problem of flocculation and deformation from the influence of crosslinked [9−16]. However, there are no reports on the seeded dispersion process through the monomer absorption procedure prior to polymerization in the presence of crosslinked. In this work, PMMA crosslinked was carried out with divinylbenzene (DVB).

Experiment :

Materials:

The monomers, including methyl methacrylate (MMA) 99.5 % , and DVB (80%) and methacrylic acid (MAA) were obtained from the Al-adadin industrial corporation (Shanghai, China) and sinopharm Chemical Reagent Co.Ltd China. Potassium persulfate as the initiator was obtained from the sinopharm Chemical Reagent Co.Ltd China .Toluene (C_7H_8) 92.14%,and Tetrahydrofuran (C_4H_8O),99.0 %, for treatement ,were obtained from Shanghai ,Lingfeng Chemical ,Reagent Co and sinopharm Chemical Reagent

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Co.Ltd China . Ltd.These chemicals were used as received. Deionized water was used for the experiment.

PMMA Synthesis :

PMMA nanoparticles were synthesized by soap-free emulsion polymerization in a three-necked flask equipped with a reflux condenser and a mechanical stirrer. A typical synthesis of poly(methyl methacrylate) (PMMA) nanoparticles is as follows:

20 mL of monomer (MMA) and 200 mL water were added to the three necked

flask, and were stirred at 300 rpm under N_2 gas . The mixture was refluxed , and after the mixture had boiled for 3 min, then 0.2 g potassium persulfate powder was added to the solution. Temperature of the reaction was fixed at 80 ^{0}C, and then reaction was stopped after 2 hours. After cooling the solution it was centrifuged at 10,000 rpm for 10 minutes to precipitate the PMMA nanoparticles and washed three times with deionized water and recycle ultrasonic and centrifuged .The PMMA nanoparticles were dried in oven at 60 ^{0}C for 24 hours .

Cross-linking of PMMA nanoparticle

We found that boiling medium polymerization can also be used for the synthesis of highly cross-linked polymer nanoparticles. As these nanoparticles are stable to organic solvents, they have applications in cases when organic solvents are necessary, such as for bioanalysis. A typical synthesis of highly cross-linked PMMA nanoparticles is as follows:

25 ml monomers (MMA) , 0.25 ml MAA and cross-linker 3.75 ml (DVB) were mixed together with 200 mL of deionized water in 250mL a three-necked flask equipped with a condenser and mechanical stirrer. The mixture was stirred at a speed of 300 rpm and heated to boiling point. After 5 min of boiling, 0.25 g of potassium persulfate was added. The reaction was stopped after 2

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hours at 100 ^{0} C . PMMA cross linked nanoparticles were washed three times with deionized water and recycle ultrasonic and centrifuged .The PMMA cross-linked nanoparticles were dried in oven at 60 ^{0}C for 24 hours .

Preparation of PMMA Membrane and Opal Film :

Non-cross-linked and cross-linked PMMA nanoparticles were used for the fabrication of Membrane and opal film. The Membrane as well as opal film were composed of non-cross-linked and cross-linked nanoparticles. It was found that nanoparticles with cross-linkages are 13 % stable to organic solvents such as toluene or Tetrahydrofuran (THF). In typical membrane and opal film synthesis procedure, 0.325 g PMMA nanoparticles with 0.325 g PMMA Crosslinked treated with 5 mL (Toluene or Tetrahydrofuran THF) for 3 to 7 days. The membrane and opal film structure were observed after the treatment of Toluene or Tetrahydrofuran (THF). The main reason for the formation of non-close-packing can be ascribed to the swelling behavior of the cross-linked nanoparticles during vapour treatment [17 - 31] .

SEM Results :

Silicon wafer was cut into (3mm x 3mm) pieces and Piranha solution [32] was used for cleaning Silicon wafer . Then followed by triple rinsing in ethanol with ultrasonic cleaning for 30 min then nitrogen (N_2) was used for drying . Then small amount of sample was placed on Si wafer for SEM test .

TEM Tests :

For TEM Test , a small amount of sample was dissolved in test tube and 3mL of deionized water was added to it and the solution was stirred by ultra-sonication to make sure the sample was dissolved . Then 10 µ L solutions was transferred to clean copper grid and kept for drying for TEM test.

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UV Results :

For UV results, a small amount of sample was put in test tube and then was dissolved in 3mL deionized water into the sample and the mixture was stirred by ultra-sonication to make sure the sample was uniform . Then it was transferred to cavity of spectrophotometer machine to get the test. Spectra were recorded at 400 to 750 nm.

Results and Discussion :

The FSEM photos (A ,B and C) show uniform structure and clear from those photos size of PMMA nanoparticles is about ….

The FSEM photos (D and E) crosslinked PMMA nanoparticles show uniform structure .The TEM photos (F ,G and H) show uniform structure, distribution .The FSEM images (N and O) membrane treated by Tetrahydrofuran (THF) show smooth surface .

The FSEM images (Q ,P and S) and images of membrane treated by Toluene show smooth surface and good enhancement of smooth and good membrane .The FSEM images (T and W) and images show very clear and uniform opal film structure by treated by toluene .

Figure 1. U.V. spectra have shows maximum absorbance at 460 nm for PMMA nanoparticles.

Figure 2. U.V. spectra shows maximum absorbance at 480 nm for PMMA Crosslinked nanoparticles.

Figure 3. U.V. spectra shows maximum absorbance at 400 nm for membrane treated by Tetrahydrofuran **(** THF).

Figure 4. U.V. spectra showed maximum absorbance at 540 nm for Opal film treated by Toluene .

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Conclusions :

1. we have developed new synthesis method of soap-free emulsion polymerization for highly crosslinked PMMA Nanoparticles. By raising the emulsion polymerization temperature to the boiling point, polymer nanoparticles have been obtained in a short reaction time using a simple experimental set-up.
2. The FSEM and TEM images of PMMA nanoparticles showed crosslinked results have showed structure and uniform structure which is clear from Image .
3. The FSEM and TEM images of their membrane treated with toluene shows smooth surface and good enhancement and gives uniform opal films.
4. The FSEM and TEM images membrane treated with THF have given no opal structure .
5. U.V. Results have showed absorption at 400 -750 nm.

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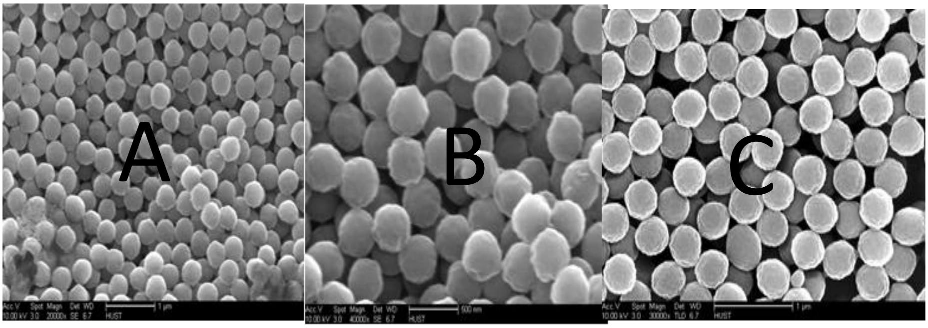

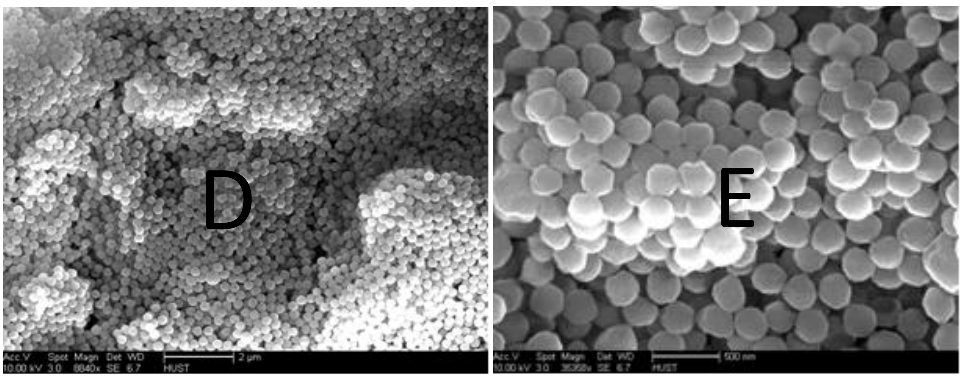

Photo FSEM (D and E) of Crosslinked PMMA nanoparticles

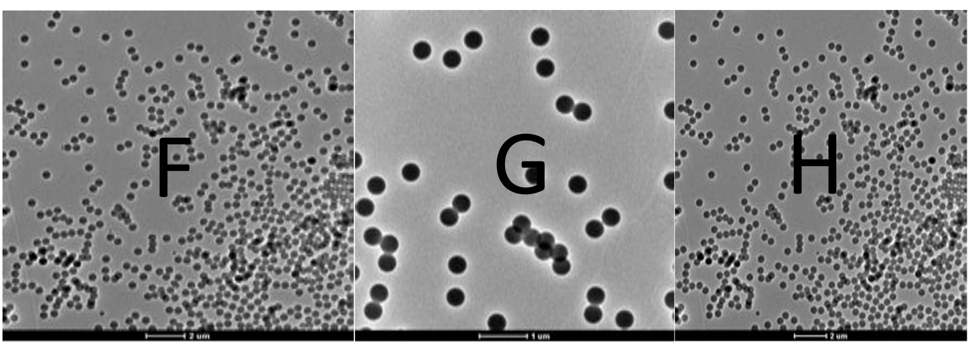

Photo (F ,G and H) TEM of PMMA nanoparticles

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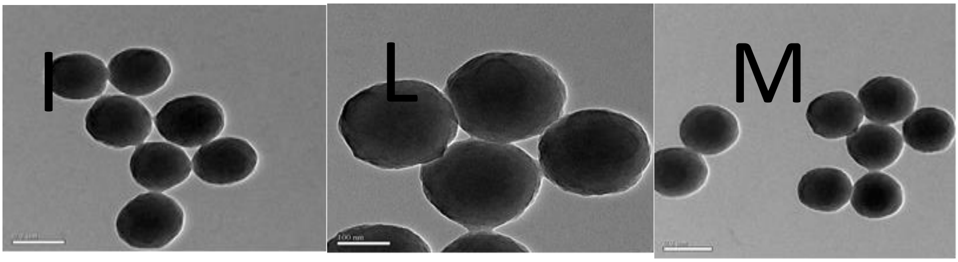

Photo (I ,L and M) TEM of Crosslinked PMMA nanoparticles

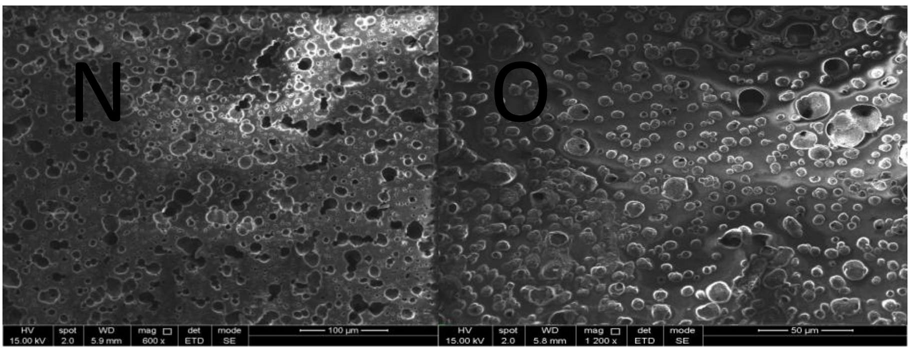

Photo (N and O) FSEM of Membrane of PMMA &PMMA crosslinked treated THF

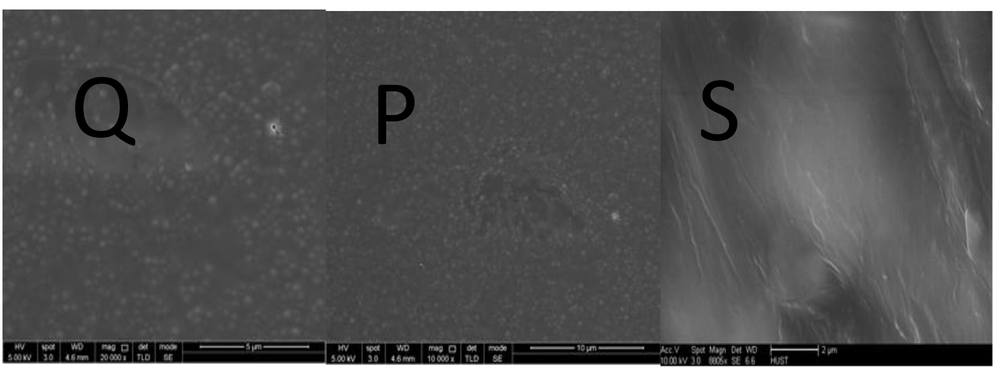

Photo (Q ,P and S) FSEM of Membrane of PMMA &PMMA crosslinked treated Toluene

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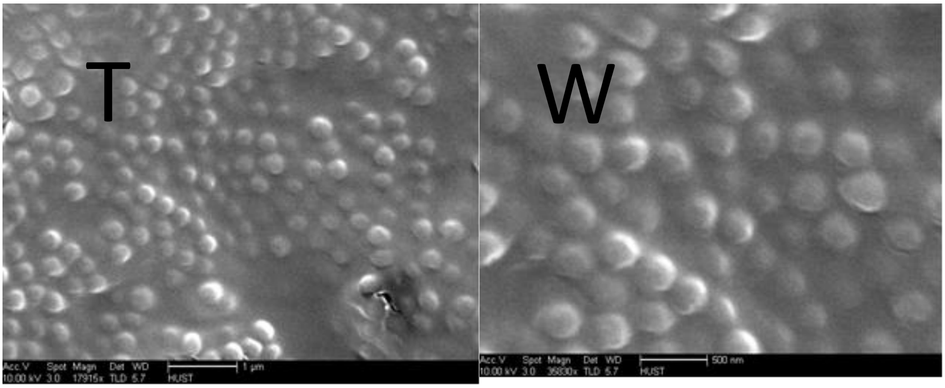

Photo (T and W) FSEM of Opal Film

Photo.20 : Opal film 0.325 g PMMA+0.325 g PMMA Cross +5 mL THF)

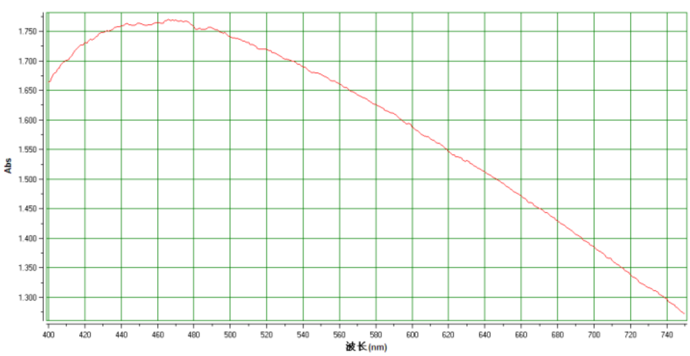

Fig .1. U.V of PMMA nanoparticles

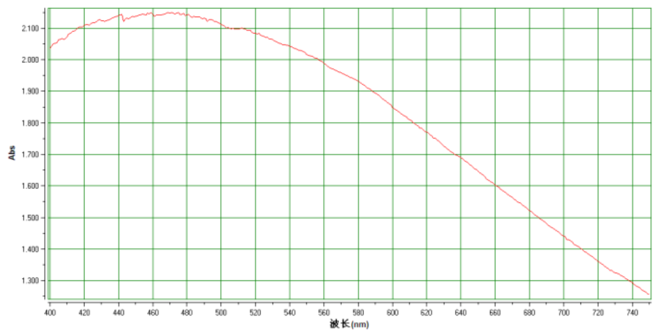

Fig .2 . U.V of PMMA nanoparticles Cross linked.

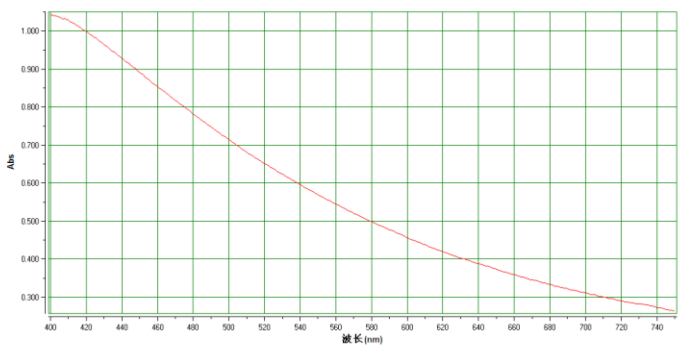

Fig .3 . U.V of Membrane treated Tetrahydrofuran

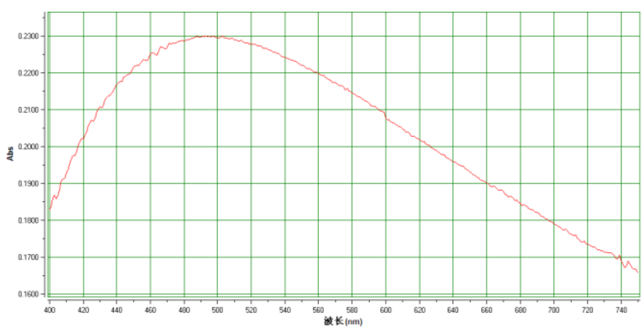

Fig .4 . U.V of Opal film treated Toluene