The Physical Properties of Nonionic Waterborne Polyurethane with a Polyether as Side Chain

Bing Li, Dan Peng, Ning Zhao, Qiuhong Mu, Jinhui Li

New Material Institute, Shandong Academy of Sciences, Jinan, Shandong, China

Correspondence to: B. Li (E-mail: mindless000cn@163.com)

ABSTRACT: A series of nonionic waterborne polyurethanes (WPU) based on hydrogenated methylene diphenylene diisocyanate, polybutylene succinate diol, polybutylene adipate diol, polyethylene glycol, and diethylene glycol as chain extender were synthesized with a polyether, MPEG-$(OH)_2$, as side chain. The physical properties such as tensile strength, elongation, hardness, molecular weight, kinetic viscosity, and so on were detected. The WPUs made with polyesters have the best tensile strength but the lowest elongation. Because of the hydrophilic property of MPEG-$(OH)_2$ grafted on the WPUs, they have obvious increases of solid contents and water absorptions with the ratio of MPEG-$(OH)_2$. The functional group ratio of NCO/OH is another reason affecting the hydrophilic properties of the WPUs. In addition, the water ratios of the dispersions dramatically affect the stability of WPU systems. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Waterborne resins were used increasingly in accordance with the requirement of volatile organic compounds-free materials, motivating the research and development of waterborne polyurethane.[1] As for a material with excellent properties in variety of aqueous-based resins, waterborne polyurethane plays important role in leather coating agent, breathable fabric, adhesives, and specialty chemicals.[2,3]

The excellent performance of waterborne polyurethane is mainly related to the special structures of the periodic backbone and functional side chains.[4] Typically, the linear waterborne polyurethanes are synthesized by the prepolymerization of soft segments such as polyester diols and polyether diols and rigid monomers, for example, diisocyanates, chain extenders, anionic, cationic, and nonionic functional diols.[5,6] In the process of chain extension reaction, the low molecular weight diols and diamines are chain extenders which react with residual isocyanates on the end of the polyurethane prepolymer molecules.[7–9] In the case of a trifunctional group chain extender being adopted, the crosslinked structure polyurethane is achieved. Primarily due to the alternating structure of soft and hard segments on backbone of polyurethane, it is obvious that some special properties are presented. The hard segments, originated from the isocyanates and low molecular weight diols, tend to be

microphase separating with the temperature decrease in the process of polyurethane membrane forming.[9,10] The soft segments impart the elastomeric properties to polyurethane. The microphase separation phenomenon in the alternating structure of soft and hard segments enforces various characteristics of polyurethane such as the physical, mechanical, and adhesive properties which depend strongly on the degree of phase separation between hard and soft segments.

Self-emulsification of the resulting polyurethane plays a dominant role in the preparation of waterborne polyurethane. It is different from emulsion polymerization adopting emulsifier that the functional monomers, that is, anionic, cationic, or nonionic diols and diamines provide emulsification effect for the stable waterborne polyurethane system. As in the case of conventional anionic waterborne polyurethanes, the dimethylolpropionic acid (DMPA) is the commonly used functional monomer. The waterborne polyurethanes, by varying the ratio of DMPA to the other segments in the backbone, present a wide range of hydrophilic properties which severely affect the solid contents of them.

Various types of diisocyanates, dios, and chain extenders as well as different functional monomers can be used to synthesize waterborne polyurethane. As results of different ratios of alternating soft segments to hard ones and construction of widely

different structures of waterborne polyurethane back-bone, the materials can be hard and brittle, soft and tacky, or anywhere in between. The waterborne polyurethane with DMPA as functional monomer has higher adhesive property but lower water resistance than nonionic waterborne polyurethane. In addition, nonionic waterborne polyurethane is the best breathable coating agent in variety of waterborne polyurethanes.[11–13]

Anionic polyurethane dispersions are widely used materials in fields of adhesives, coating agents, and so on. Nonionic polyurethanes, however, are more difficult to dispersing in water because of the weak hydrophilic character of the nonionic functional segments on backbone of polyurethanes. Recently, several scientists focused on the preparation and application of nonionic waterborne polyurethane which has hydrophilic side chains contributing to the stability of it in water system and simultaneously improving other mechanical properties.[14–17] This article provides a convenient tactic that prepares a polyether with diols on chain end, which can react with isocyanates as a nonionic functional monomer. The physical properties of prepared nonionic waterborne polyurethane such as the tensile strength, elongation, solid content, and so on were detected.

EXPERIMENTAL

Reagents

The following reagents were used in waterborne polyurethane synthesis: hydrogenated methylene diphenylene diisocyanate (HMDI, Wanhua), polybutylene succinate diol (PBSD, $M_w = 2000$, Wanhua), polybutylene adipate diol (PBAD, $M_w = 600$, Wanhua), polyethylene glycol (PEG, $M_w = 1000$, Wanhua), diethylene glycol (AR grade, aldrich), dibutyltin dilaurate (DBTDL, AR grade, Aldrich).

The self-emulsification of nonionic polyurethane depends on the hydrophilic character of nonionic monomer, so before the PU synthesis, the nonionic monomer grafting on the side chain of PU must be synthesized first. This step started from the 2,2-dimethoxypropane (AR grade, Aldrich) protection to the diols of DMPA (AR grade, Aldrich). About 1 mol of DMPA was dissolved in acetone (AR grade, Sigma) in which there were 0.1 mol of p-toluene sulfonic acid (AR grade, Aldrich) and 1.2 mol of 2,2-dimethoxypropane dissolving. After reacted for 12 h at N_2 atmosphere, the products were separated through column chromatography (silica gel) and dried in vacuum for 12 h, and then reacted with monomethoxypolyethylene glycol (MPEG, $M_w = 2000$, Wanhua) with 4-dimetylaminopyridine (AR grade, Across) as catalyst, dicyclohexylcarbodiimide (AR grade, Aldrich) and dichloromethane(AR grade, Aladin) as solvents. The residue was separated with column chromatography (silica gel) and dried for 12 h. The deprotection to diols was carried out in chloride acid (AR grade, 37 wt %, Aladin) and methanol (AR grade, Aladin) atmosphere at 50°C, and the end product MPEG-$(OH)_2$ which was a polyether with diols on chain-end was accepted. The synthesis process was shown in Scheme 1. This terminal product was characterized in terms of ^{13}C- and ^{1}H-NMR (Avance APX400, Bruker).
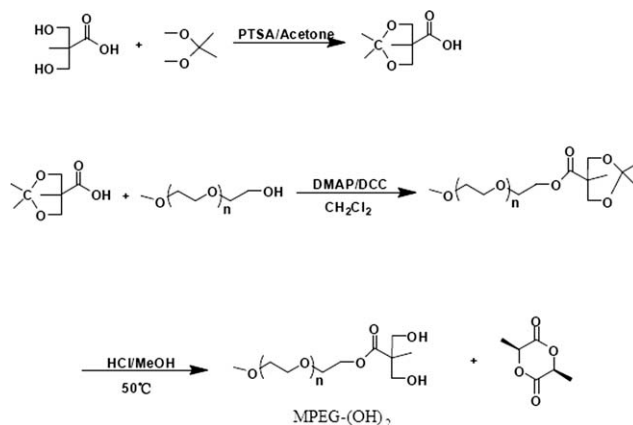
Scheme 1. The preparation process of nonionic diol MPEG-$(OH)_2$.

Prepolymer Preparation and Chain Extension

The nonionic WPU was prepared in a water-free environment avoiding the reaction between the isocyanates and water molecules. Before the self-emulsion of WPU in water, for purpose of sufficient reaction of nonionic functional MPEG-$(OH)_2$ and isocyanates, the prepolymer of WPU was prepared first. The dehydration was carried out in a vacuum environment at 110°C, and the quantitative MPEG-$(OH)_2$, PBSD, (or PBAD and PEG as well as a definite quantity of the above polyether and polyester's mixture) were added in a flask. About 2 h later, a corresponding quantity of HMDI and a drop of DBTDL were added. The reaction were implemented at 80°C.

After 4-h prepolymerization, another copolymerized monomer, diethylene glycol, was added with the reacting temperature at 60°C as the chain extending stage, and some acetone was added for decreasing the viscosity of the material. After another 4 h reaction, the polyurethane was accepted completely.

Self-Emulsion of PU

Before emulsifying in water, about 30 g of nonionic PU was added in a stainless steel vessel. High speed stir of 4000 rpm was provided with a stirrer (FARFLY), and the quantitative water was added in gradually. About 30 min later, this process was accomplished and the WPU was prepared.

Physical Properties Testing of WPU

The nonionic WPU is a widely used material for fabric surface modification, so the physical properties are relatively important for its application. WPU films were obtained by casting it on glass surface and dried at room temperature for 7 days and at 50°C for 24 h. After demolding from the glass surface, the films were kept in a vacuum drying oven avoiding moisture in air.

The mechanical properties were performed by a universal testing machine (WDW-5, Times Shijin Instrument).

The water absorption rate of films was tested by a method that the films were immersed in water and stored for 24 h. Water was wiped off from the surface of the films and they were weighted immediately (this method conforms to the industrial
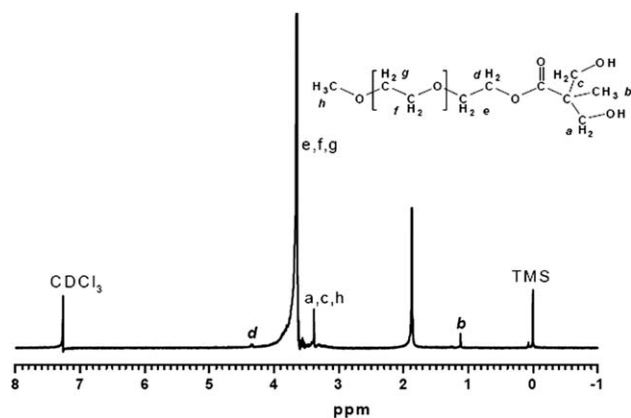
Figure 1. The ^{1}H-NMR spectra of MPEG-$(OH)_2$.

Figure 2. The ^{13}C-NMR spectra of MPEG-$(OH)_2$.

standard of China, HG 2-1612-85). Equation 1 gives the water absorption rate (W):

$$W = \frac{G_2 - G_1}{G_1} \times 100$$

The G_1 is the weight of film preimmersed in water and the G_2 is that postimmersed in water 24 h later.

The hardness of films was detected with a shore hardness instrument (LD-J, Haibao Instrument) according to the relevant standard, GB/T 533-1999.

The solid content of the dispersion was detected by drying it at 80°C for 3 days and calculating the weight ratio of residue to the dispersion.

About 2 mg WPU films were dissolved in 1 mL of tetrahydrofuran at 25°C for 48 h, for molecular weight test. The molecular weights (M_n and M_w) and polydispersity indexes (PDIs) of the five WPUs were recorded on a Waters 1525 gel permeation chromatographer (GPC) instrument with three gel columns (7.8 × 300 mm^2) and a differential refractive-index detector and ultraviolet detector. The eluent was tetrahydrofuran at 35°C with a flow rate of 1.0 mL/min^{-1}.

The kinetic viscosities of WPU dispersions were tested according to the kinetic viscosity testing standard of China, GB/T265-1988.

RESULTS AND DISCUSSION

Identification and Analysis of the Synthesized MPEG-$(OH)_2$
The MPEG-$(OH)_2$ was synthesized by the esterification of MPEG and diol-protected DMPA and the subsequent depro-
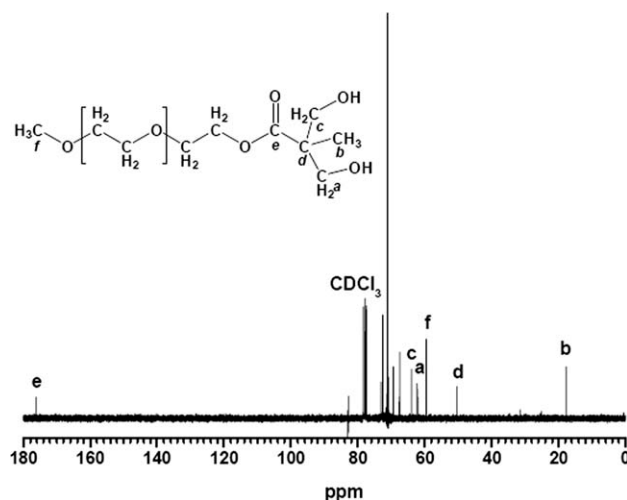
tection to diol. The ^{1}H-NMR of MPEG-$(OH)_2$ is shown in Figure 1. The new proton signal appearing at $\delta = 4.30$ ppm represents the esterification of carboxyl of diol-protected DMPA and hydroxyl of MPEG. The signals of $\delta = 3.40$ and 1.10 ppm are the proton resonances of —CH_2— and —CH_3 on DMPA. The hydrogen signal on two methyls of protected diol disappeared, which represents the deprotection of hydroxyl on the end product MPEG-$(OH)_2$. Figure 2 displays the ^{13}C-NMR of MPEG-$(OH)_2$ on which the $\delta = 17.8$, 50.3, 63.9, 67.5, and 176.1 ppm are the resonances of —CH_3, —C—, —CH_2—, —CH_2—, and —CO— on MPEG-$(OH)_2$. There is no signal between 20 and 25 ppm proving the deprotection to diol on MPEG-$(OH)_2$.

Mechanical Properties of WPU
Table I displays five different WPU dispersions with various polyester, polyether diols, and mixture of them, the functional group ratio, NCO/OH and the weight ratio of MPEG-$(OH)_2$ to all monomers before dispersing in water. For stability of WPU system, the different ratios of functional nonionic monomer MPEG-$(OH)_2$ were used. Up to now, the excellent mechanical properties of PU that provide obvious tensile and elongation are the most interesting aspects to scientists. The WPU also has the special properties in these items. The tensile strengths and elongations of the prepared five WPUs were listed in Table II. Generally speaking, the WPU made by polyester has higher strength but lower elongation than that made by polyether.[4] The prepared WPUs obey this rule, that is, WPU1 and WPU2

Table I. The Components of the WPUs

| WPU sample | HMDI | Diols | | | | | NCO/OH | Ratio of MPEG-$(OH)_2$ (wt %) |
		PBSD	PBAD	PEG	MPEG-$(OH)_2$	Diethylene glycol		
WPU1	11.94	20			6	2.12	1.30	14.97
WPU2	15.94		12		4.5	2.12	1.39	13.02
WPU3	16.96			15	9	2.12	1.53	20.89
WPU4	21.21	20		7.5	9	2.12	1.70	15.20
WPU5	16.96		6	7.5	9	2.12	1.44	21.64

Table II. The Physical Properties of the WPUs

| WPU sample | Tensile strength (MPa) | Elongation (%) | Shore A hardness | Water absorption (W%) | Solid content (%) | Molecular weight | | PDI |
						M_n	M_w	
WPU1	25.9	870	57	11.21	20.8	23,467	34,149	1.45
WPU2	30.6	642	68	12.12	17.44	20,775	32,781	1.58
WPU3	6.59	1229	42	25.37	19.45	14,009	18,211	1.30
WPU4	18.14	1112	47	39.43	31.56	10,276	17,990	1.75
WPU5	10.92	1422	45	34.82	26.03	15,181	21,662	1.43

made by PBSD and PBAD have the obvious tensile strengths than those made by PEG only or the mixture of them, and oppositely the elongations of them are the lowest. In a general way, the ester groups on the backbone of WPU enforce the tensile strength because of the ester groups' structure and steric hindrance between them. Figure 3 represents the tensile strength-elongation of the five WPUs. The tensile strengths of the five WPUs increase with the elongations, but there is no yield for them.

The shore A hardness of the five WPUs were shown in Table II. Just like the trend of the tensile strength, the hardness increases with the ratio of polyester diols in them, nevertheless, they are not hard enough compared with the WPUs with anionic functional monomers. This may be the long side chain steric effect of nonionic MPEG-$(OH)_2$.

In terms of solid content and water absorption shown in Table II, there are different presentations for the five WPUs with different ratios of MPEG-$(OH)_2$. The WPUs containing polyester diols have lower water absorption, but the solid contents of them are also lower than those with polyether diols. The WPUs with the mixture of polyester and polyether diols have the highest items of solid contents and water absorptions. As a general rule, the ester groups on backbone of WPU molecules are more hydrophilic than ether groups. However, in this experiment, the solid contents and water absorptions of WPUs conflict to this rule. Table I also gives

out the NCO/OH and weight ratios of MPEG-$(OH)_2$ in all the monomers. These two aspects of three WPUs with PEG are some bigger degrees than those of the other two WPUs with polyester only. This may be the main reason that they have higher solid contents and water absorptions than those with ester groups. The content of functional nonionic monomer MPEG-$(OH)_2$ being a surfactant is the important item affecting the solid content and water absorption. It is another reason affecting the hydrophilic property of WPU that the molecular weight of WPU decreases with the ratio of HMDI.

Table II also gives out the molecular weights and PDIs of the five WPUs, which are tested with GPC. The number average molecular weights (M_n) and weight average molecular weights (M_w) are in scales of 1×10^4–2.4×10^4 and 1.8×10^4–3.4×10^4, respectively. The PDIs are close to 1.5. The relationship between NCO/OH and M_n or M_w of five WPUs is shown in Figure 4. The two lines are linear fit lines corresponding to relative parameters of M_n and M_w. It is commonly accepted that the M_n and M_w decrease with increase in ratio of NCO/OH. The trend presented in Figure 4 is in accordance with this rule.

It is important to some degree that a suitable viscosity of WPU dispersion is convenient for application, but the viscosity of WPU dispersion is too high to be stably stored for long time. So, it is reasonable keeping the stability of WPU dispersion first. The five WPU dispersions were stored for 6 months at room
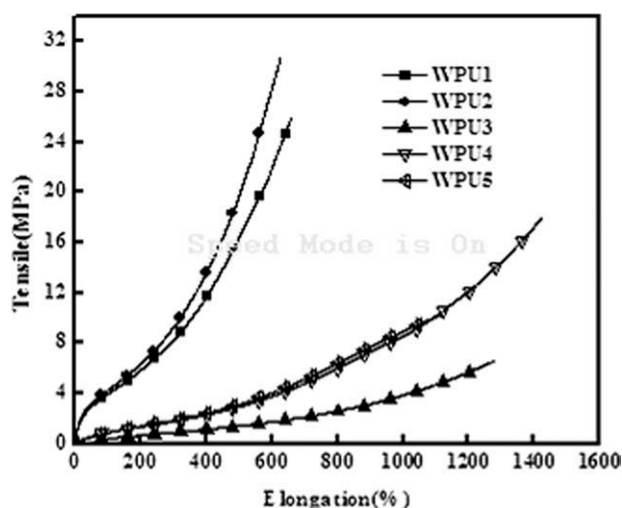
Figure 3. The tensile strength-elongation of the WPUs.
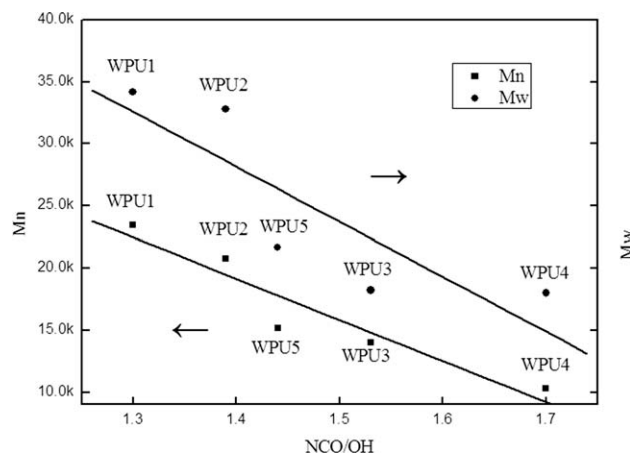
**Figure 4.** The relationship of NCO/OH and M_n or M_w of the WPUs.
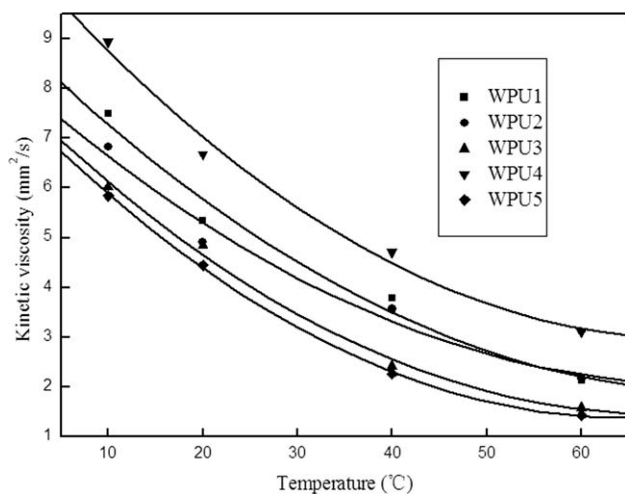
Figure 5. The kinetic viscosities of the WPU dispersions with temperature increase.

temperature and it is obviously that there is no great change in viscosities. The kinetic viscosities of WPU dispersions with temperature increase are presented in Figure 5. The five lines are polynominal fits to different viscosities of WPU dispersions. It is a nonlinear decreasing trend with temperature increase. Figure 6 shows the viscosity increases of WPU dispersions with water ratios. The kinetic viscosities increase greatly when water increases a little amount. The high viscosities of WPU dispersions are unfavorable for stability of them. It was seemed as stable systems that the water ratios keep in the scale of Figure 5, because of uniformity of viscosities prestorage and poststorage of 6 months.

CONCLUSIONS

A nonionic functional monomer, MPEG-$(OH)_2$ was synthesized by reaction of MPEG and 4-dimethylaminopyridine DMPA and deprotection to dimethylol on DMPA. The five nonionic WPUs
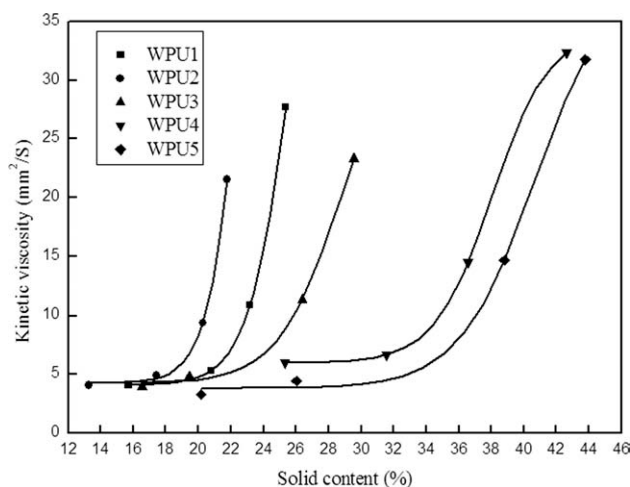
Figure 6. The viscosity increases of the WPU dispersions with water ratios.

were prepared with MPEG-$(OH)_2$ as the nonionic functional monomer.

WPU1 and WPU2 made by PBSD and PBAD have the obvious tensile strengths than those made by PEG only and the mixture of them, and oppositely the elongations of them are the lowest. The tensile strengths of the five WPUs increase with the elongations, but there is no yield for them. In addition, they are not hard enough compared with the WPUs with anionic functional monomers which may be the effect of long side chain soft character of nonionic MPEG-$(OH)_2$. Because of the hydrophilic property of MPEG-$(OH)_2$ grafted on WPU, they have obvious solid content and water absorption increases with the ratio of MPEG-$(OH)_2$. In addition, the content of HMDI in them is another reason that affects the hydrophilic properties of them because of molecular weight decreases with its increase.

The five WPUs described in the experiment are stable dispersions comparing with those that have low water ratio, because increase of kinetic viscosities will cause the instability of WPU dispersion.

REFERENCES

1. Zhu, X. L.; Jiang, X. B.; Zhang, Z. G.; Kong, X. Z. *Prog. Org. Coat.* **2008**, *62*, 251.

2. Kim, B. K.; Shin, J. H. *Colloid Polym. Sci.* **2002**, *280*, 716.

3. Hirose, M.; Kadowaki, F.; Zhou, J. H. *Prog. Org. Coat.* **1997**, *31*, 157.

4. Madbouly, S. A.; Otaigbe, J. U. *Prog. Polym. Sci.* **2009**, *34*, 1283.

5. Dieterich, D.; Keberle, W.; Witt, H. *Angew. Chem.* **1970**, *9*, 40.

6. Seneker, S. D.; Rosthauser, J. W.; Markusch, P. H. Polyurethanes 92: Proceedings of the 34th SPI Annual Tech/Mark Conference, New Orleans, Louisiana. **1992**, 588.

7. Visser, S. A.; Cooper, S. L. *Macromolecules* **1991**, *24*, 2576.

8. Kim, B. K.; Kim, T. K.; Jeong, H. M. *J. Appl. Polym. Sci.* **1994**, *53*, 371.

9. Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

10. Narayan, R.; Chattopadhyay, D. K.; Sreedhar, B. *J. Appl. Polym. Sci.* **2006**, *99*, 368.

11. Jhon, Y. K.; Cheong, I. W.; Kim, J. H. *Colloid Surf. A.* **2001**, *179*, 71.

12. Chen, G. N.; Chen, K. N. *J. Appl. Polym. Sci.* **1997**, *63*, 1609.

13. Dieterich, D.; Keberle, W.; Wuest, R. *J. Oil Colloid Chem. Assoc.* **1970**, *53*, 363.

14. Tsai, H. C.; Hong, P. D.; Yen, M. S. *J. Appl. Polym. Sci.* **2008**, *108*, 2266.

15. Yen, M. S.; Tsai, H. C.; Hong, P. D. *J. Appl. Polym. Sci.* **2006**, *100*, 2963.

16. Yen, M. S.; Tsai, H. C.; Hong, P. D. *J. Appl. Polym. Sci.* **2007**, *105*, 1391.

17. Yen, M. S.; Chen, P. Y.; Tsai, H. C. *J. Appl. Polym. Sci.* **2003**, *90*, 2824.