

## 트리메틸로일프로판 가교제에 의한 양이성 폴리우레탄 분산 입자의 제조 및 특성

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(2016년 3월 3일 접수, 2016년 5월 30일 수정, 2016년 7월 16일 채택)

## Synthesis and Properties of Cationic Polyurethane Dispersions: Influence of the Content of Trimethylolpropane as Inner Crosslinker

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(Received March 3, 2016; Revised May 30, 2016; Accepted July 16, 2016)

**Abstract:** A series of water dispersible polyurethanes containing quaternary ammonium group as the hydrophilic group with different content of trimethylolpropane (TMP) as inner crosslinker were prepared. IR spectroscopy was adopted to demonstrate the polymerization reaction and structure of polymer. The effects of TMP content on PU properties were investigated. Particle size distribution (PSD) analysis and morphology of PU observed by TEM showed that particle size of PU dispersions initially decreased and then increased with increasing TMP content. The viscosity of the PU dispersions with TMP addition was bigger than the PU dispersions without TMP. TG analysis indicated thermal stability and microphase separation degree of PU was enhanced with increasing TMP content. Contact angle and gel content of PU also increased as increasing TMP content. Meanwhile, tensile strength increased and then decreased with the increment of TMP content.

**Keywords:** cationic polyurethane, crosslinker, particle size distribution, thermal stability, microphase separation.

### Introduction

Aqueous polyurethane (PU) dispersions have gotten extensive application in various fields such as adhesives or coatings for various substrates, including textile fabrics, plastics, wood, glass fibers, and metals.<sup>1-5</sup> Aqueous PU dispersions can be classified into ionic and nonionic types. Nonionic types contain hydrophilic soft segment pendant groups such as polyethylene oxide,<sup>6</sup> whereas the polymer chains of ionic types contain anionic or cationic centers. These centers could be pendant acid or tertiary nitrogen groups which are neutralized to form salts.<sup>7-10</sup> Cationic PU dispersions show very high adhesion to various ionic substrates, especially anionic substrates such as leather or glass.<sup>11,12</sup> However, anionic PU dispersions

have been frequently reported and investigated in the literature and there are only few reports on cationic PU dispersions.

Aqueous polyurethanes are known to be environment-friendly materials with elasticity, good adhesion, and chemical resistance.<sup>13-16</sup> However, some properties of waterborne polyurethane such as water resistance and weather resistance need to be improved further. In order to improve the water and weather resistance of the polyurethane dispersions, the most common method is to form crosslinked structure in PU.<sup>17-19</sup>

In this article, aqueous cationic polyurethane dispersion was prepared by introducing tertiary amine group to endow polyurethane chain with self-emulsifying ability in water and using trimethylolpropane (TMP) as inner crosslinker. In general, TMP influence is reported in some papers usually just as a small part of one paper, the emphasis is often placed on the chain extenders and nNCO/OH. In our work, we made a comprehensive study on the influence of TMP as inner crosslinker. This paper focused on the effects of the TMP content on the

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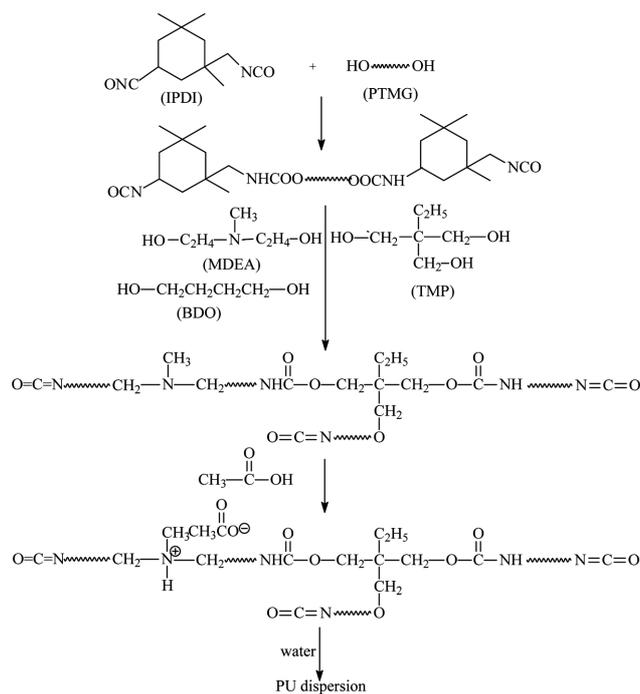
PU dispersions properties such as the particle size distribution, viscosity and the morphology. At the same time, the effects of the TMP content on contact angle, mechanical and thermal properties of the emulsion-casting films were investigated.

## Experimental

**Materials.** Polytetramethylene ether glycol (PTMG,  $M_n = 1000$  g/mol) was dried at 60 °C under vacuum before use. Isophorone diisocyanate (IPDI), *N*-methyldiethanolamine (MDEA), 1,4-butanediol (BDO), trimethylolpropane (TMP), acetic acid (HAc), *N*-methyl-2-pyrrolidone (NMP) and dibutyltin dilaurate (DBTDL) are of analytical grade and used without further purification.

**Preparation of PU Dispersion.** Synthetic route of preparation of aqueous PU dispersion was depicted in Scheme 1. Briefly, a 500 mL round-bottomed, four-necked flask was equipped with a mechanical stirrer, thermometer, condenser, and a dropping funnel. The reaction was carried out in a constant temperature oil bath. First, the mixture of PTMG1000 and IPDI was heated at 80 °C for 2.5 h to obtain NCO terminated prepolymer. Afterwards, the system was cooled to 70 °C and DBTDL was added as catalyst. The solution of MDEA, BDO and TMP in NMP was added and the reaction was kept for 2 h under constant stirring. Then the polyurethane prepolymer temperature dropped to 40 °C, and the tertiary amine groups were neutralized by the addition of acetic acid, and the degree of neutralization was 100%. The mixture was stirred for further 30 min to ensure the reaction was completed. Then, the prepolymer were dispersed by adding distilled water to the prepolymer solution under vigorous stirring. Samples were prepared by adjusting the TMP content at fixed cationic content and fixed R (NCO/OH ratio) which are shown in Table 1.

**Characterization of Latex Particles and Films.** Fourier transform infrared (FTIR) spectra were recorded on a VETOR-2 fourier transform infrared spectrometer (Bruker Company, Germany) in the range from 4000 to 400  $\text{cm}^{-1}$  in transmission. The particle size and its distribution of the synthesized latex



**Scheme 1.** Formation of PU dispersion.

were measured by Nano-ZS particle sizer (Malvern Instruments Company, UK). The viscosity of the PU dispersions was measured by DV-III rheometer (Brookfield Company, USA). Transmission electron microscopy (TEM) micrographs of the particles were taken with H-600 transmission electron microscope (Hitachi Company, Japan) with an acceleration voltage of 200 kV. The samples were stained with 2% phosphotungstic acid (PTA) solution. Thermogravimetry (TG) analysis of the polymer film was performed on a Q500 thermogravimeter (TA Instruments Company, USA) under the nitrogen atmosphere at a heating rate of 10 °C/min from 20 to 600 °C. Contact angles (CA) were measured by the sessile drop method at room temperature, using a JC2000A contact angle goniometer (Shanghai Zhong Chen Powereach Co., China). Static contact angles were obtained from liquid droplets on the surface of latex films. Tensile strength was measured by TS 2000-S tensile strength testing machine (Gotech Testing Machines Inc., Tai-

**Table 1.** Feed Compositions of Dispersion Polyurethanes Synthesized with Various Amounts of TMP

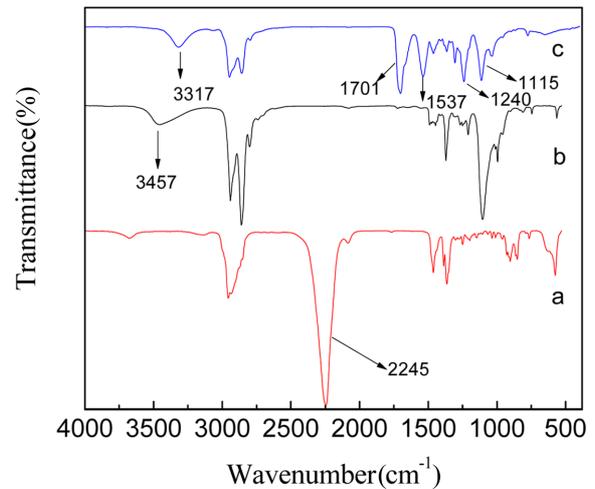
Sample	IPDI(g)	PTMG1000(g)	MDEA(g)	BDO(g)	TMP(g)	Content of TMP(%)
PU1	17	12	2.86	1.62	0	0
PU2	17	12	2.86	1.08	0.54	1.61
PU3	17	12	2.86	0.81	0.81	2.41
PU4	17	12	2.86	0.54	1.07	3.20

wan). Crosslinking density was measured by using gelling data. The mass of initial polyurethane film coated with filter paper was  $W_1$ . The film was extracted continuously in a Soxhlet extractor for 24 h, then was dried to get the film, and the mass of which was  $W_2$ . According to Formula (1), the crosslink density was calculated by gel content.

$$\text{Gel content} = W_2/W_1 \quad (1)$$

## Results and Discussion

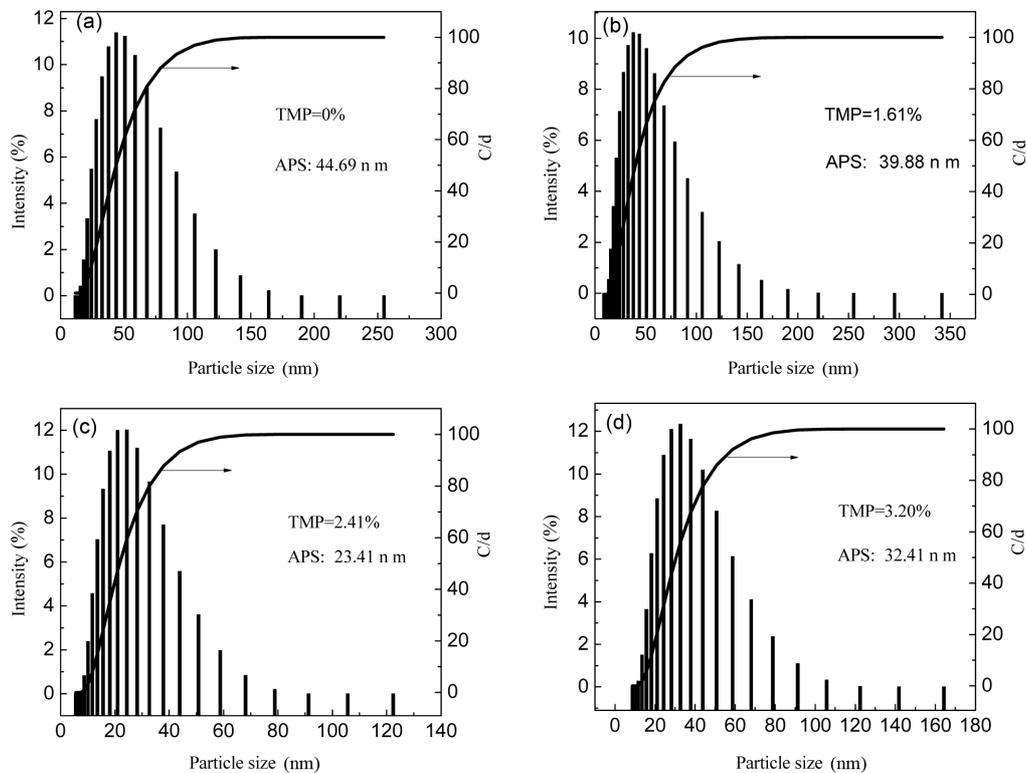
**IR Spectroscopy.** IR spectra of IPDI, PTMG1000 and the PU obtained from the cast film are shown in Figure 1. The disappearance of the  $\nu$  NCO at  $2245 \text{ cm}^{-1}$ , the disappearance of the  $\nu$  OH at  $3457 \text{ cm}^{-1}$  and the appearance of  $\nu$  N-H at  $3000\text{--}3400 \text{ cm}^{-1}$  in Figure 1(c) demonstrate the formation of the pre-designed PU. IR Spectrum of PU also contains all the related information of the primarily structure of the final polymer. The characteristic absorption bands at  $3317$  and  $2946 \text{ cm}^{-1}$  are corresponding to the stretching of hydrogen bonding of N-H band and  $-\text{CH}_2$  asymmetric stretching respectively. The bands at  $1701 \text{ cm}^{-1}$  (amide I,  $\nu\text{C}=\text{O}$ ),  $1537 \text{ cm}^{-1}$  (amide II,  $\delta\text{N-H}$  and



**Figure 1.** FTIR spectra of IPDI (a); PTMG1000 (b); PU (c).

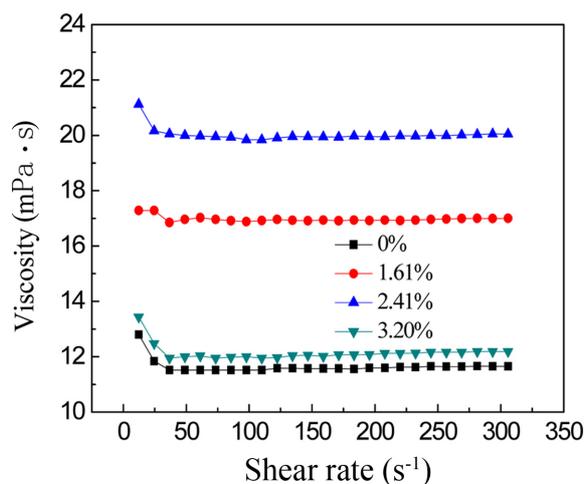
$\nu\text{C-N}$ ),  $1240 \text{ cm}^{-1}$  (amide III,  $\nu\text{C-N}$  and  $\delta\text{N-H}$ ) and  $1115 \text{ cm}^{-1}$  (antisymmetric  $\nu\text{C-O-C}$ ) are also observed. These vibrations are also strong evidence for the formation of PU.

**Particle Size and Viscosity.** Figure 2 shows the particle size distribution and the average particle size (APS) of PU with different content of TMP (In these samples, the NCO/OH ratio



**Figure 2.** Particle size distributions of PU dispersions with different contents of TMP: (a) TMP=0%; (b) TMP=1.61%; (c) TMP=2.41%; (d) TMP=3.20%.

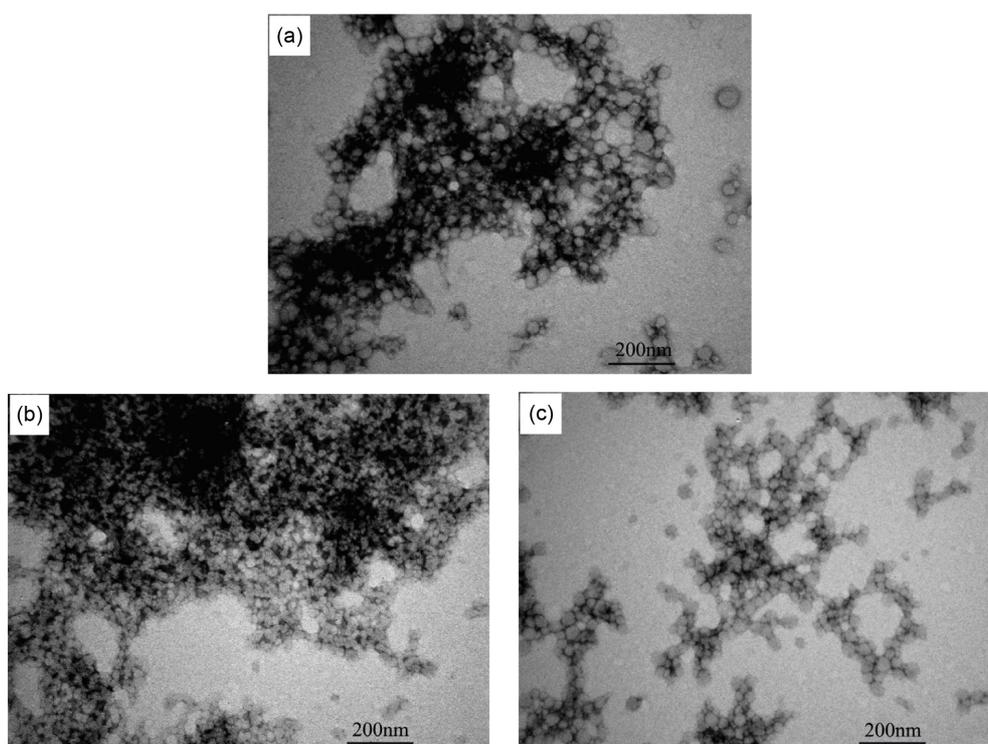
was kept constant). Although TMP increases the crosslinking of PU prepolymer, resulting in the decrease in flexibility of molecular chain and the increase in the viscosity of prepolymer, which may make the particle size of PU dispersions increase, in our study it is seen that the particle size decreases from 44.69 to 23.41 nm with the increasing of TMP amount from 0% to 2.41%. Based on the literature recordation, the particle size not only depends on the chain rigidity and viscosity caused by increasing TMP, but also relies on other factors such as -NCO reaction sensitiveness, phase separation and regularity of macromolecule chains.<sup>20</sup> When small quantity of TMP was added, the micromolecular movement was restrained by the certain crosslink network and the reaction sensitiveness between the water and the remnant -NCO in prepolymer decreased. The decrease of the reaction sensitiveness leads to the decrease in the content of the hard urea bonds, which has high polarity making the dispersion difficult. Therefore, with the addition of small quantity of TMP, the content of hard urea bonds decreases and the particle size becomes smaller. However, the particle size increases from 23.41 to 32.41 nm with the increasing of TMP amount from 2.41% to 3.20%. This increase may be due to the further increased viscosity which makes the emulsification more difficult when the TMP content is beyond



**Figure 3.** Viscosities of PU dispersions with different contents of TMP.

a certain extent.

Figure 3 shows the viscosity of PU dispersions with TMP content. Each particle in the dispersion is absorbed by a thin layer of water due to the presence of hydrophilic quaternary ammonium groups on the surface of the particles. With a decrease in the size of the polymer dispersion particles, the relative size of the water layer to total particle size increases.



**Figure 4.** TEM photograph of PU dispersions with different contents of TMP: (a) TMP=0%; (b) TMP=2.41%; (c) TMP=3.20%.

According to the theory of Mooney, the emulsion viscosity increases. From Figure 3 it can be seen that the PU viscosity increases due to the decrease of the PU particle size caused by the introduction of TMP.

**TEM.** The morphology of PU dispersion particles under 100000 magnification was observed by TEM as shown in Figure 4. The particle is spherical and we can directly observe that the PU particle size decreases with the introduction of TMP at first, and then increases with the TMP amount increase. The changing trend is consistent with the results obtained by particle size distribution analysis. At the same time, Figure 4(c) shows that PU with high TMP content is well dispersed as an emulsion. The reason maybe is that the PU particles are not easy to lead to adhesions between each other with the increase of the crosslinking degree.

**TG.** TG curves of the samples as a function of TMP content are shown in Figure 5. The initial decomposition temperature ( $T_{d,onset}$ ), the temperature 50% decomposition ( $T_{d,1/2}$ ), and the temperature at the maximum rate of decomposition ( $T_{d,max}$ ) for different samples are listed in Table 3. The TGA studies of the PU films shows that the degradation of PU films starts at

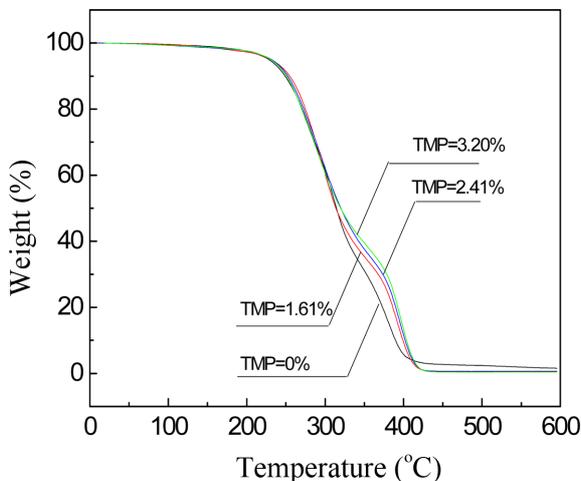


Figure 5. TG curves of the PU films with different contents of TMP.

Table 2. TGA Data of PU with Different Contents of TMP

The content of TMP	$T_{d,onset}$ (°C)	$T_{d,1/2}$ (°C)	$T_{d,1max}, T_{d,2max}$ (°C)
0%	228	315	312, 380
1.61%	231	314	297, 393
2.41%	232	320	295, 395
3.20%	231	320	289, 397

Note:  $T_s$ ,  $T_{50}$  and  $T_{max}$  refer to the temperature at weight loss of 5%, 50% and maximum decomposition of the polymer, respectively.

Table 3. Contact Angle, Tensile Strength and Gel Content of PU Films with Different Contents of TMP

Sample	The content of TMP (%)	Contact angle (°)	Tensile strength (MPa)	Gel content (%)
PU1	0	58.61	3.33	43.6
PU2	1.61	65.60	12.47	87.3
PU3	2.41	66.34	10.79	90.3
PU4	3.20	67.52	4.21	93.2

beyond 228 °C. It can be seen from Figure 5 and Table 2 that the thermal stability of PU films increases by increasing the content of TMP. There are obvious two degradation stages in Figure 5. The early stage degradation occurred mainly in the hard segments where urethane groups first undergo depolymerization and the second stage degradation occurred mainly in the soft segments. The  $T_{d,1max}$  and  $T_{d,2max}$  in Table 3 are corresponding to the temperature at which the weight loss of hard segments and soft segments reaches to their maximum respectively. It can be seen in Table 3 that the difference between  $T_{d,1max}$  and  $T_{d,2max}$  become larger with the increase of the TMP content in PU, which reflects that the microphase separation degree increases with increasing TMP content.

**Contact Angle.** The contact angle measurements of PU films with different content of TMP are shown in Table 2. As it can be seen, there is a remarkable increase in contact angle when TMP is introduced into PU. The contact angle increases from 58.61° to 67.52° as increasing TMP content from for 0% to 3.20%. This suggests that the hydrophilicity and chain flexibility decreases with increasing content of TMP. The chain rigidity caused by introduction of TMP does not allow the cationic groups to move towards the film-air surface. Furthermore, TG analysis above has showed the microphase separation degree increased with increasing TMP content. With the microphase separation, soft segments migrate to the air surface, while the hard segments with hydrophilic groups migrate toward the bulk and aggregate closer to the interface at the substrate surface,<sup>21</sup> therefore, the contact angle on the air surface film increases.

**Mechanical Properties.** The mechanical properties of PU films with respect to TMP content are shown in Table 2. It can be seen that the tensile strength increases when introducing the TMP in PU as intercrosslinker. PU2 and PU3 show the larger tensile strength compared with the others. The tensile strength of PU4 decreases to 4.21 MPa, it can be concluded that the tensile strength of PU decreases when the content of TMP is

beyond certain extent.

**Gel Content.** The gel content increases with the TMP content. Moreover, it is worth noting that PU1 without TMP is 43.7%, indicating that PU1 is still endowed with a low cross-linking density even if no trifunctional TMP is incorporated. This may be attributed to the crosslinking caused by hard-hard segment or hard-soft segment hydrogen bonding.

## Conclusions

Aqueous polyurethane dispersions were synthesized from IPDI, PTMG1000, MDEA, 1,4-BDO and different content of TMP. The effects of TMP content on particle size distribution, viscosity, latex morphology, contact angle, mechanical and thermal properties were studied and discussed. Average particle size of polyurethane dispersions decreased with the introduction of TMP at first. But with further increase in TMP content, the particle size then increased. Viscosity of the PU dispersions with TMP was bigger than the PU dispersions without TMP. Tensile strength increased and then decreased with increasing TMP content. Thermal stability and micro-phase separation degree, contact angle, gel content of PU increased with the increment of TMP content.

**Acknowledgements:** We would like to express our great thanks to the National Natural Science Foundation of China (grant number: 51603117), the Research Fund of Education Department of Shaanxi Provincial Government (grant number: 2014JK1106) and the Natural Science Foundation for doctor of Shaanxi University of Science & Technology (BJ12-27) for financial support.

## References

1. H. C. Wu, Z. G. Li, L. Bai, and J. Y. Gu, *J. Macromol. Sci., Pure Appl. Chem.*, **52**, 847 (2015).
2. D. Kim, G. Kim, G. Song, and I. Chung, *Polym. Korea*, **40**, 216 (2016).
3. Y. K. Yang, N. Kwak, and T. S. Hwang, *Polym. Korea*, **29**, 81 (2005).
4. Y. H. Guo, J. J. Guo, H. Miao, L. J. Teng, and Z. Huang, *Prog. Org. Coat.*, **77**, 988 (2014).
5. Z. F. Wu, H. Wang, X. Y. Tian, M. Xue, X. Ding, X. Z. Ye, and Z. Y. Cui, *Polymer*, **55**, 187 (2014).
6. T. Shen, Y. Sun, C. Sun, and M. Lu, *Polym. Korea*, **37**, 232 (2013).
7. H. G. Im, H. S. Lee, and J. H. Kim, *Polym. Korea*, **31**, 543 (2007).
8. Y. J. Kim and B. K. Kim, *Colloids Surf. Sci.*, **292**, 51 (2014).
9. M. M. Rahman, I. Lee, H. H. Chun, D. K. Han, and H. Park, *J. Appl. Polym. Sci.*, **131**, 1001 (2014).
10. M. Akbatsin, M. E. Olya, M. Ataefard, and M. Mahdavian, *Prog. Org. Coat.*, **75**, 344 (2012).
11. P. Z. Li, Y. D. Shen, X. W. Yang, and G. H. Li, *J. Polym. Res.*, **19**, 9786 (2012).
12. H. Daemi, R. R. Rad, M. Barikani, and M. Adib, *Appl. Catal. A-Gen.*, **468**, 10 (2013).
13. C. Philipp and S. Eschig, *Prog. Org. Coat.*, **74**, 705 (2012).
14. S. W. Zhang, J. F. Chen, D. Han, Y. Q. Feng, C. Shen, C. Chang, Z. L. Song, and J. Zhao, *J. Coat. Tech. Res.*, **12**, 1 (2015).
15. H. J. Naghash and E. K. Naeni, *Polym. Korea*, **35**, 409 (2011).
16. H. Daemi, M. Barikani, and M. Barmar, *Carbohydr. Polym.*, **92**, 490 (2013).
17. K. K. Jena, R. Narayan, and K. V. S. N. Raju, *Paint India*, **61**, 56 (2011).
18. D. W. Kang, S. W. Park, D. W. Kang, and S. W. Par, *Polym. Korea*, **35**, 488 (2011).
19. D. Y. Yang, L. Han, H. Q. Zhang, and F. X. Qiu, *J. Macromol. Sci., Pure Appl. Chem.*, **48**, 277 (2011).
20. V. E. Mona, B. Mehdi, and S. M. S. Mohammad, *Iran. Polym. J.*, **15**, 323 (2006).
21. L. Lei, Z. B. Xia, C. B. Ou, L. Zhang, and L. Zhong, *Prog. Org. Coat.*, **88**, 155 (2015).