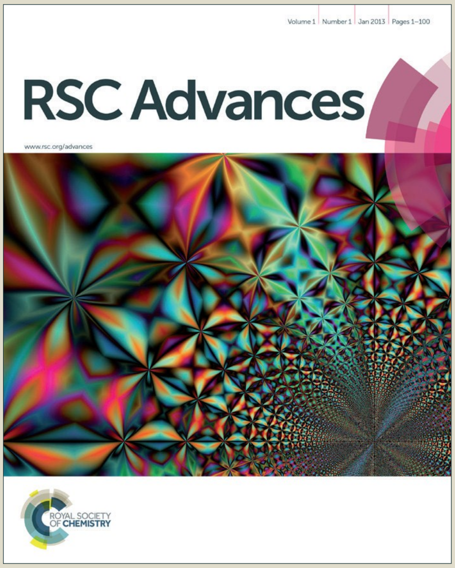
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Novel Amphoteric Polyurethane Dispersions with Postpolymerization Crosslinking Function Derived from Hydroxylated Tung Oil: Synthesis and Properties

Zhiyong Ren*, Lu Liu, Huafen Wang, Yang Fu, Lei Jiang, Baixia Ren

High & New Technology Research Center of Henan Academy of Sciences,
Zhengzhou 450002, P. R. China

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Novel hydroxylated tung oil-based amphoteric polyurethane polymer dispersions (HTO-AmPUDs) having postpolymerization crosslinking capability were synthesized and found to be reversibly stable in both acidic and basic media. Reactive HTO-AmPUDs showing surface activity and film properties adjustable with crosslinking extent are potentially new polymeric components and surfactants in polymer alloys synthesis.

1. Introduction

Possible depletion of fossil feedstocks during next century[1] will force conversion to biosourced starting materials for production of many polymer families[2], including the highly versatile polyurethanes[3], where feasible. Moving to natural feedstocks and to waterborne systems instead of those based on volatile and more hazardous organic solvents will also have environmental benefits. Accordingly, research on polyurethanes based on new polyols from natural vegetable oils is becoming increasingly important. So far, hydroxyl-modified soybean oil (prepared by using the reaction sites of carbon-carbon double bonds in triglycerides) and its application in thermosetting polyurethane foam have been well studied,[4,5] the hydroxyl-modified tung oil prepared in the same way has also shown utility in composites.[6] Among the many available polyols[7] derived from fossil and natural oils, the hydroxyl-modified tung oil or hydroxylated tung oil (HTO) prepared by using ester alcoholysis or aminolysis is unique in that its molecular structure features two primary hydroxyl groups and a hydrocarbon chain containing three conjugated double bonds. Tung oil therefore can be readily incorporated into a thermoplastic polyurethane composition, including polyurethane water borne dispersion (PUD).

PUDs have many advantages, especially their environment-friendly characteristics. However, drawbacks of PUDs include poor water and solvent resistance as well as the relative softness and weakness of polymer films made from their emulsions. Therefore PUDs are not generally competitive with fossil fuel derived products in terms of these properties. Incorporation into the urethane polymer of hydrophobic vegetable oil structures such as HTO, where postpolymerization crosslinking is possible, is thus expected to be one of the more effective ways to overcome these disadvantages. And the HTO based anion PUDs[8-9] have shown some good properties.

PUD can be categorized into anionic, cationic, amphoteric and non-ionic types depending on the structures of the chain extenders used in polyurethane synthesis. Each type has its own characteristics and can be used in different applications. Of these types, anionic PUD is the type that has been mostly studied[10] whereas amphoteric PUD is the most difficult to be synthesized. In limited studies on amphoteric PUD, the focus of the research was on protein resistance[11-12], isoelectric points (IEP)[13], multi-shape memory effects and self-healing properties[14]. To the best of our knowledge, however, there are no reports on amphoteric PUD based on HTO. Since it combines the properties of anionic with cationic types, amphoteric PUD especially the HTO-based amphoteric PUD (HTO-AmPUD), is expected to have wider and unique special applications, possibly including functionality as a specialty polymeric surfactant. For this reason we chose to study the utility of tung oil in crosslinkable polyurethanes, especially AmPUD and in addition because it is a natural material found in abundance in China.

Therefore, in the present work, the latest research results on emulsion and film properties for HTO-AmPUD are first provided. To this end, we designed and successfully synthesized a series of novel HTO-AmPUDs having postpolymerization crosslinking functionality. The structure, emulsion properties such as IEP, applicable pH range, particle size, surface tension, and critical aggregation concentration (CAC) were characterized and analyzed. We also preliminarily

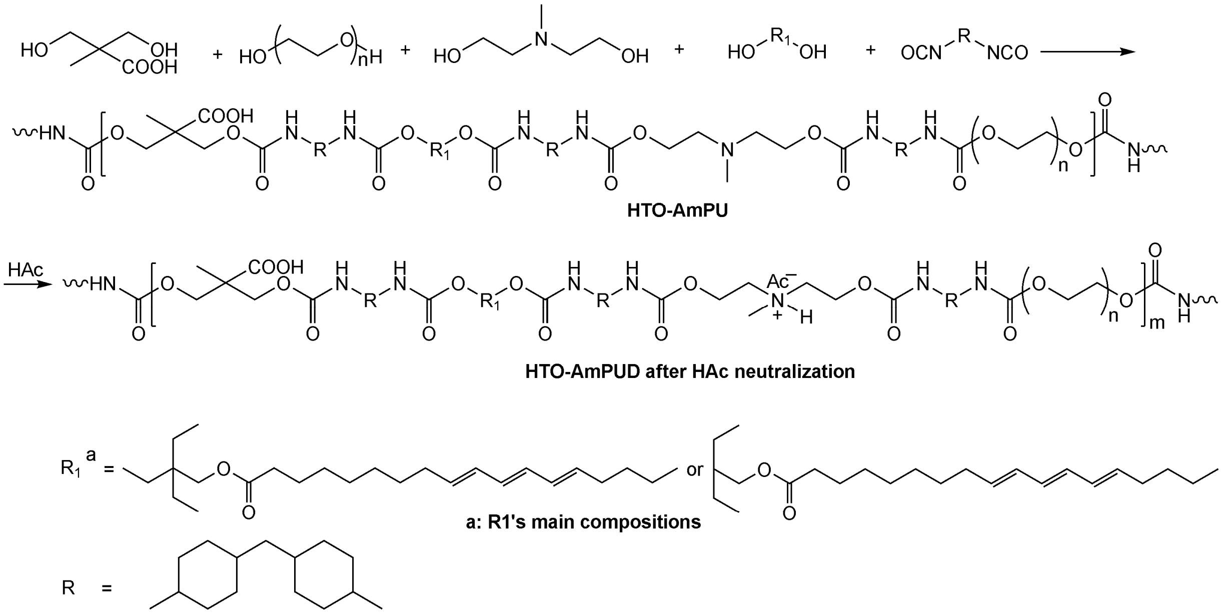


Figure 1. Structural scheme of HTO-AmPUD

Table 1. Formula and basic properties of HTO-AmPUD samples

Samples	HTO-AmPUD -0	HTO-AmPUD -1	HTO-AmPUD -2	HTO-AmPUD -3
f[A/B/C/D/][a]	3/3/3/2[e]	3/3/3/2	3/3/3/4	3/3/3/6
HTO content (w%)	0	12.9	19.0	24.7
M_n [b]	7300	7200	7900	7400
M_w/M_n [b]	1.4	2.1	2.6	2.4
Z-Average(nm) [c]	91	198	112	64
Zeta potential (mv) [c]	21.1	18.0	18.8	19.2
Surface tension (mN/m)[d]	39.2	41.7	41.0	40.2

[a] The monomer ratios in feed (mol/mol). A: DMPA; B: MDEA; C: PEG; D: HTO (except HTO-AmPUD-0)
[b] Determined by GPC using DMF as the fluent. [c] Determined at pH = 4.3. [d] Determined at pH = 4.7. [e] PPG

studied the effect of the triene crosslinking reaction on mechanical properties and solvent resistance of films made from the emulsions.

The HTO-AmPUD should be advantageous, with its more hydrophobic character and postpolymerization crosslinking ability, as compared with common AmPUD. These features make it not only a type of novel polymer, but also a new potential polymeric emulsifier that can be further used in polymer alloys preparation, as HTO-AmPUD itself can function as one reactive component in such alloys. We think it may open a new train of thought for better utilization of the natural tung oil resource and to develop a novel type of reactive amphoteric polymer.

2. Experimental section

Several HTO-AmPUDs with different amounts of hydrophobic and hydrophilic content were synthesized, using HTO as the hydrophobic/postpolymerization crosslinking component, and incorporating three other components: nonionic hydrophilic polyethylene glycol (PEG) with molecular weight of 800, anionic and cationic chain extenders dimethylol propionic acid (DMPA) and N-methyldiethanolamine (MDEA). The diisocyanate used was 4,4 methylene dicyclohexyl diisocyanate (HMDI) in all cases. The HTO-AmPUD was composed of the hydrophobic triene donor HTO (Figure S1, Supporting Information). Polypropylene glycol (PPG) with molecular weight of 400, which is similar to that of HTO, was used to synthesize PPG-AmPUD as a control to show the function of HTO.

Figure 1 and Table 1 show the structural scheme as well as the formula and basic properties of HTO-AmPUD samples prepared in the present paper. HTO-AmPUDs with different HTO content were designated as HTO-AmPUD-1, HTO-AmPUD-2, and HTO-

AmPUD-3 where the larger numbers correspond to higher HTO content. Details on raw materials, synthesis, structure and some properties characterization are seen in the Supporting Information.

3. Results and Discussion

3.1. Structural characterization

Both FTIR (Figure S2, Supporting Information) and NMR (Figure S3, S4, Supporting information) results combined with our previous work[15-16] show that the conjugated double bonds as well as the three water borne components have been successfully introduced to the polyurethane chain. GPC data for HTO-AmPUD with different HTO content and for the control sample PPG-AmPUD show (Table 1) that all the HTO-AmPUDs and PPG-AmPUD show similar average molecular weight around $7\text{-}9\times10^3$g/mol. The HTO-AmPUD neutralized by acetic acid is stable at pH = 4.0-4.5 at room temperature for at least one year.

3.2 Emulsion properties

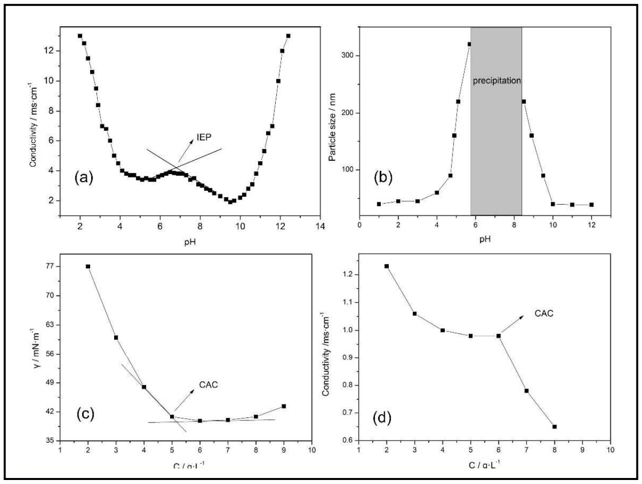


Figure 2. Emulsion properties of HTO-AmPUD-1
(a) IEP from conductometric titration curves; (b) Z-Average versus pH value; (c) CAC from conductivity curve; (d) CAC from surface tension curve.

Figure 2 shows some of the basic emulsion properties including IEP, applicable pH range and surface tension values in HTO-AmPUD-1. The obtained IEP is 6.7 for HTO-AmPUD-1 as Figure 2(a) shows. In order to further study the effect of other influencing factors on the IEP in HTO-AmPUD, we prepared HTO-AmPUDs with different acid-base ratios (COOH/-N(CH_3)-), and different HTO content. Properties were also measured for PPG-AmPUD (no HTO incorporation) for comparison.

The results (Table 1S, Supporting information) show that the IEP moves to lower pH value as the alkaline group content increases. When the ratio of COOH/-N(CH_3)- reaches 1:2 from 1:1, HTO-AmPUD shows the characteristic of a cationic emulsion, namely it could not be dispersed in alkaline water. In another respect, the measured IEP of the “X-AmPUD” system hardly changed when X=PPG was replaced by X=HTO, nor with increasing X=HTO content. The nature of the precipitate at IEP, however, was different with different ‘X’ groups: the PPG-AmPUD is a paste, while the HTO-AmPUD precipitate is particulate. These results suggest that although the incorporation of HTO into polyurethane does not affect IEP, it does change the molecular interaction due to presence of the long aliphatic branched chain. Further investigation of these phenomena is being conducted.

Figure 2(b) shows the variation of particle size with pH in the range 1.5~12.0 for HTO-AmPUD-1. In acid medium, the average particle size increases with increasing pH value. When pH value reaches 4.9, the particle size markedly increases and precipitate begins appearing at pH = 5.6. As titration with sodium hydroxide aqueous solution continued, the amount of precipitate increased, reaching a maximum at pH = 6.5. Thereafter the precipitation volume decreased, with complete water dispersion at pH = 8.5. After that, the particle size continued decreasing with increase of pH value, until about pH = 10, where particle size stabilized at about 30-40 nm. This result shows that the applicable range of pH for HTO-AmPUD-1 emulsion stability is 1.5~5.6 under acidic conditions and 8.5~12.0 in alkaline conditions. It was also found that the stable HTO-AmPUD emulsion can be repeatedly converted from acid to base and from base to acid medium, which shows that such an amphoteric polyurethane dispersion has excellent reversibility.

It is seen from Table 1 that the average particle size (at pH = 4.3) increases from 91 nm (control sample PPG-AmPUD, without HTO) to 198, and then from 198 to about 64 nm with the increase of HTO content from 12.9% to 24.7%. This result shows that incorporation of HTO at relatively low content increases the particle size, which is reasonable considering the long side chain in HTO; when HTO content is further increased, the interaction among the hydrophobic chains would be stronger inside the micelle, leading to the decrease of particle size.

Figure 2(c) and 2(d) show CAC results for HTO-AmPUD-1 obtained by two methods, which give the similar CAC values with 6 g/L by conductivity and 5 g/L by surface tension. Considering the molecular weight of HTO-AmPUD is around 8000g/mol and the surface tension can be 40 mN/m, HTO-AmPUD shows certain surface activity. If further considering its postpolymerization crosslinking function, HTO-AmPUD is expected to be a potential novel reactive polymer emulsifier for use in polymer alloy preparation. Further research work in this respect is currently being conducted.

The comparative surface tension arising from different HTO content (Table 1) shows that the surface tension increased a bit from 39.2 to 41.7 mN/m when PPG was replaced with HTO; when HTO content was increased from 12.9% to 24.7%, the surface tension decreased a bit from 41.7 mN/m to 40.2 mN/m.

3.3. Stress-strain and dynamic properties of HTO-AmPUD cast film

Another purpose of incorporating HTO into polyurethane is aimed at improving and adjusting mechanical properties as well as improving water and solvent resistance for HTO-AmPUD film, as the amphoteric polyurethane film itself is a type of polymer material. Figure 3 shows the strain-stress curves and dynamic properties of the HTO-AmPUD-1 film under different heat treatment conditions.

It is clearly seen from Figure 3(a) that the mechanical properties have significant changes when films are subjected to heat treatment at different temperatures. For the initial film (after heating at 60^{o}C), the tensile strength HTO-AmPUD is relatively low (5.2MPa) but elongation is relatively long (216%); after heat treatment at 120^{o}C for 30 minutes, breaking tenacity has obviously increased, rising from 5.2 to 20.3 MPa while the elongation decreased to 166%; after heat treatment at 150^{o}C, the tensile strength increased to 24.3 MPa while elongation has again decreased. Meanwhile, it is clearly seen from Figure 3(b) that the storage modulus *E'* and loss factor tan δ are different from the heat treatment at different temperatures. Also as the relaxation peak increases from 26°C (initial film) to 42°C (after heat treatment at 120^{o}C) and 45°C (after heat treatment at 150^{o}C), *E'* rises from 13.4 to 285.1 MPa, and further to 315.2 MPa accordingly.

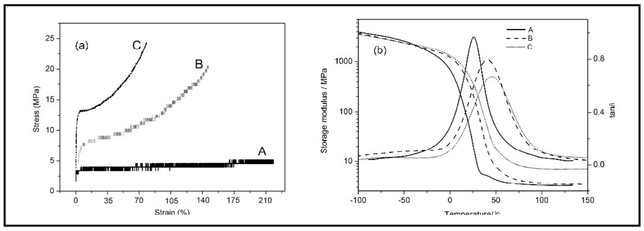


Figure 3. Stress-strain and dynamic properties of the HTO-AmPUD films after heat treatment at different temperatures (A: initial film; B: 120^{o}C; C: 150^{o}C)

It is worth noting that in order to make comparison with the control sample PPG-AmPUD (without HTO) in mechanical properties upon heat treatment, we subjected a PPG-AmPUD sample to the same temperatures, at 120^{o}C and 150^{o}C. Unfortunately, the dumbbell-shaped test sample softened under such high temperature, which prevented strain-stress testing. This is in accordance with the low heat resistance of the common low molecular weight polyurethanes (our sample ~ 7000 g/mol). Further, this sample contained no double bond structure so was incapable of any heat-induced crosslinking reaction. This result is additional evidence that it is the double bond postpolymerization that gives HTO-AmPUD tolerance to 150^{o}C and increases its tenacity.

3.4. Resistance to solvents

In addition to mechanical properties, we also investigated the effect of heat treatment on solvent resistance for HTO-AmPUD-1 and its control sample PPG-AmPUD. Five types of solvents including toluene and benzene (aromatic solvents), ethyl acetate (esters), ethanol and isopropanol (alcohols) as well as acetone (representing ketones) and N-methyl pyrrolidone (representing amide solvents) were selected to do the rubbing solvent resistance. These solvents cover the change from non-polarity to polarity, representing the five most commonly used categories.

It can be observed (Table 2S, Supporting information) that PPG-AmPUD without HTO, even after the heat treatment at all three temperatures, could hardly withstand exposure to any of the solvents. Exposed films would either break or dissolve or undergo surface changes, although the extent of surface destruction would be reduced with increasing heat treatment temperature. This is not too surprising since the PPG-AmPUD is incapable of heat-induced crosslinking. For HTO-AmPUD-1 under the same heat treatment, however, the resistance to solvents has been much improved. Except in alcohol and NMP (well recognized as an excellent polymer solvent) in which the film treated at 90^{o}C was a bit affected, HTO-AmPUD-1 film treated at 120^{o}C already has excellent resistance to all the five types of solvents.

3.5. Double bond reaction with heat treatment

The above results are expected to be closely related to the reaction of double bonds in HTO-AmPUD during the heat treatment at different temperatures. The reaction of these double bonds (Figure 5S, Supporting information) has been shown by the weakening or disappearance of the band at 986cm^{-1} (belonging to conjugated double bonds) and the appearance of new bands at 1664 cm^{-1} and 1654cm^{-1}. Though these IR spectral results are quite reasonable, what we want to stress is that the properties of HTO-AmPUD film can be adjusted and controlled via the extent of double bond reaction.

The above results just show that the conjugated double bonds react to heat in HTO-AmPUD, leaving a material in which the conjugated double bonds concentration is much lower than in its raw materials HTO and tung oil. Considering that the HTO-AmPUD film is prepared as a water based emulsion, instead of in solution in an organic solvent where film is continuous on the molecular level, the feasibility of reaction of conjugated double bonds of films formed from emulsions is of important significance. Alternative ways of making conjugated double bond react in other relatively mild conditions (aside from heating) are also under investigation.

It is also worth noting that although the general oxidation mechanism for non-conjugated fatty acids has been described in detail,[17] those having conjugated double bonds appear to follow a different mechanism[18] and this mechanism needs further clarification. Therefore, the HTO-AmPUD emulsion system can serve as a new example for further studying the reaction mechanism and to establish the relationships between double bond reactions and their controlling factors as well as establishing the relationship between final emulsion film properties and the effect of crosslinking extent. We will also study other properties for HTO-AmPUD systems in the future.

4. Conclusion

Several novel HTO-AmPUD, bearing pendant conjugated triene hydrocarbon chains and containing –COOH and -N(CH_3)- groups and also incorporating 800 MW polyethylene glycol chains, were successfully synthesized. The HTO-CPUD is special for its stronger hydrophobic character and crosslinking ability, compared to common AmPUD. The HTO-AmPUD neutralized by acetic acid was found to be reversibly stable at pH = 1.5~5.6 as well as pH = 8.5~12 with the isoelectric point between pH 5.6 and 8.5 and the particle size ranging from 90 to 200 nm at pH of 4.3; the film of HTO-AmPUD can be made resistant to seven solvents of varying polarity and solvent strength, including toluene, xylene, ethyl acetate, acetone, ethanol, isopropanol and even N-methyl pyrrolidone. The breaking tenacity can be increased from 4 MPa to 24 MPa after the conjugated double bonds were partially reacted. The reactive HTO-AmPUD with around 8000g/mol plus surface tension of 40 mN/m and corresponding CAC of 6 g/L has potential as new polymeric component or surfactant for use in polymer alloys and a novel polymer material whose mechanical properties can be adjusted by controlling the extent of the postpolymerization double bond reaction.

Acknowledgements

The authors thank support from the National Natural Science Foundation of China (21074030). We would also like to express our appreciation to Dr. Han Xiong Xiao for useful discussions on experimental results, and to US A-Line Co for kindly providing TG 20C for this research.

Notes and references

No. 56 Hongzhuan Road, Zhengzhou, China. Fax: 86-371-65727239; Tel: 86-371-65511787; E-mail: zyren23@yahoo.com

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1 C. K. Williams, M. A. Hillmyer, *Polym. Rev*. 2008, **48**, 1.

2 a) S. Miao, P. Wang, Z. Su, S. Zhang, *Acta Biomater.* 2014, **10**, 1692; b) M. Alam, D. Akram, E. Sharmin, F. Zafar, S. Ahmad, *Arab. J. Chem*. 2014, **7**, 469; c) Y. Xia, R. L. Quirino, R. C. Larock, J. Renew. *Mater.* 2013,**1**, 3; d) M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chem. Soc. Rev.* 2007, **36**, 1788.

3 a) A. Saralegi, L. Rueda, B. Fernandez-d'Arlas, I. Mondragon, A. Eceiza, M. A. Corcuera, *Polym. Int*. 2013; **62**, 106; b) N. Karak. Vegetable Oil-Based Polymers, Woodhead Publishing Limited, 2012, p146–179; c) O. Kreye, H. Mutlu, M.A. Meier. *Green. Chem*. 2013, **15**, 1431; d) M. Desroches, M. Escouvois, R. Auvergne, S. Caillol, B. Boutevin, *Polym. Rev.* 2012, **52**, 38; e) G. Lligadas, J. C. Ronda, M. Galia, V. Cadiz, *Biomacromolecules*. 2010, **11**, 2825; f) Y. Lu, R. C. Larock, *Biomacromolecules.* 2008, **9**, 3332; g) B. Ni, L. Yang, C. Wang, L. Wang, D. E. Finlow, *J. Therm. Anal. Calorim.* 2010, **100**, 239; h) S. K. Lee, B. K. Kim, *J. Colloid. Interface Sci*. 2009, **336**, 208.

4 Z. S. Petrovic, *Polym. Rev*. 2008, **48**, 109.

5 D. Puthanparambila, C. Kimballa, S. L. Hsu, and Z. Ren, *Chinese J. Polym. Sci*. 2009, **27**, 447.

6 a) M. A. Mosiewicki, U. Casado, N. E. Marcovich, M. I. Aranguren, *Polym. Eng. Sci*. 2009, **49**, 685; b) U. Casado, N. E. Marcovich, M. I. Aranguren, M. A. Mosiewicki, *Polym. Eng. Sci.* 2009, **49**, 713.

7 D. P. Pfister, Y. Xia, and R. C. Larock, ChemSusChem 2011, 4, 703.

8 H. X. Xiao, U.S. Patent 7,462,679, 2008.

9 Z. X. Wang, J. T. Yuan, Q. L. Liu, X. M. Xiao, Y. H. Li, H. Chen, *Appl. Mech. Mater.* 2014, **513-517**, 251**.**

10 P. Król, B. Król, P. Holler, N. Telitsyna, *Colloid. Polym. Sci.* 2006, **284**, 1107.

11 C. Ma, H. Zhou, B. Wu, and G. Zhang, *ACS Appl. Mater. Interfaces.* 2011, **3**, 455.

12 C. Wang, C. Ma, C. Mu, and W. Lin, *Langmuir.* 2014, **30**, 12860.

13 A. Dong, G. Hou, M. Feng, A. Li, *J. Polym. Sci. Part B: Polym. Phys*. 2002, **40,** 2440.

14 S. Chen, F. Mo, Y. Yang, F. J. Stadler, S. Chen, H. Yang and Z. Ge, *J. Mater. Chem. A*. 2015, DOI: 10.1039/c4ta06304j.

15 Z. Ren, C. Zhang, L. Jiang, H. Wang, W. Zhao, F. Yang, Y. Wang, *RSC Adv.*, 2013, **3,** 17712.

16 W. Zhao, H. Wang, Z. Ren, L. Jiang, Y. Fu and X. Wang, *Magn. Reson. Chem.* 2014, online available; (wileyonlinelibrary.com) DOI 10.1002/mrc.4133.

17 Z.O. Oyman, W. Ming, R. van der Linde, *Prog. Org. Coat.* 2003, **48**, 80.

18 Z.O. Oyman, W. Ming, R. van der Linde, *Prog. Org. Coat.* 2005, *54*,198.