

Preparation of Waterborne Polyurethane Acrylate (PUA) and Application to UV-curing Coatings on the Package of Card Paper

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Abstract-In this paper, a novel waterborne UV-curing polyurethane acrylate (UV-WPUA) was prepared from toluene diisocyanate (TDI). The polyurethane acrylate resin has been synthesized by the serial steps synthetic method. The content of carboxyl group (-COOH), and molecular weight of Polyethylene glycol (PEG) and the content of unsaturated double bonds (-CH=CH₂) were optimized by the orthogonal experiment. The reaction conditions, such as order of reagent addition, neutralization agent, type of inhibitor and its water-solubility, were investigated. The resulting resin had excellent performance when the content of carboxyl group (-COOH) was 3.0 wt.%, the content of unsaturated double bonds (-CH=CH₂) was 3.0 wt.%, and molecular weight of PEG was 600. The influences of initiator content, dry time, dry temperature on UV-curing rate were discussed. The bulk performance of the resin was characterized. Flexibility, adhesion, and clarity of the UV-curing coating were excellent. The UV-curing coating of aromatic resin was successfully applied to the packaging of paper such as wine bottle label, plating-aluminum card, and cigarette case.

Keywords- UV-curing Technique; UV-curable Waterborne Aromatic Polyurethane Acrylate; Packaging of Paper; Coating Formulation; Orthogonal Experiment

I. INTRODUCTION

Due to government regulations and public environmental concerns, coatings formulators and manufacturers are seeking to implement environmentally friendly “green” coating alternatives that perform as well as or better than the conventional solvent-borne systems with mid-to-low solids [1, 2]. Additional driving forces in the industry include the increase in cost of solvents, and energy, and the need to reduce CO₂ emission. UV-curing waterborne resin systems have many advantages of low odor, non-toxicity, non-skin irritation and safer production. Therefore, it has become an attractive research and developing areas [3-6]. Radiation curable coatings based on urethane acrylate (UA) oligomers represent the major class of coatings widely used in industry [3, 4]. Such coatings are used for protection of articles and objects. In addition, they also find applications as in printing, lithography, and as adhesives. Cured coatings tend to give films a good combination of toughness, elasticity and other valuable properties. Study and improvement of properties of urethane acrylate coatings (UAC's) are of permanent interest [7-9]. Although UV-curable waterborne coatings based on acrylate functional polyurethane dispersions (UV PUDs) have found acceptance in the wood and resilient flooring markets [7, 10-14], the performance of waterborne UV technology may offer a potential for other markets as well [15-20].

In this paper, UV-curing waterborne resin was prepared from toluene diisocyanate (TDI) [21] with the synthetic formulation and the reaction conditions optimized by the orthogonal experiment. The bulk performance of the resin was characterized. The UV-curing coatings of aromatic resins with excellent flexibility, adhesion, and clarity were successfully applied to the packaging of paper.

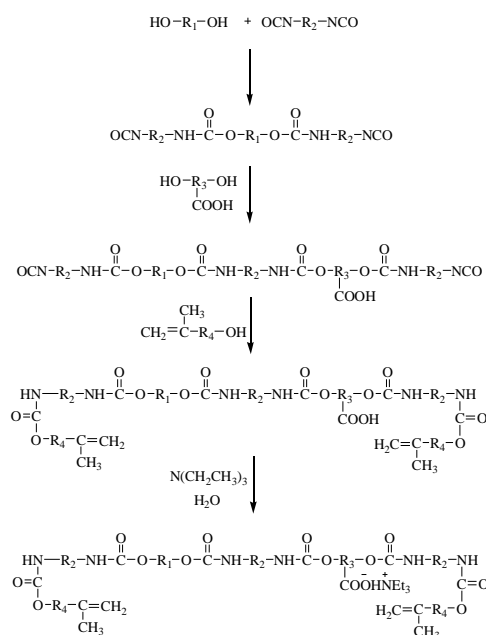
II. EXPERIMENTAL

A. Material

The toluene diisocyanate (TDI) and triethyl amine (TEA) were used as received from Yonghua Fine Chemical Co., Jiangsu, China. There are three kinds of polyethylene glycol (PEG) with different molecular weight (PEG400, PEG600 and PEG1000). Dimethylolpropionic acid(DMPA) and 1,4-butanediol(BD) were purchased from Guanghua Chemical Co., Shantou, China; 2-Hydroxyethyl methacrylate(HEMA) was supplied from SARTOMER Co., PA, USA. HEMA was purified by vacuum distillation before use. 4-(2-Hydroxyethoxy) phenyl-(2-hydroxy-2-propyl) ketone(Darocur2959) was used as an initiator, supplied from BASF; 2,2,6,6-tetramethyl-4-piperidiny-1-oxy(TEMPO) was used as an inhibitor, purchased from Wenzhou Chemical Auxiliary Co., China. All the other chemicals for synthesis were purchased from Shanghai Reagent Co., China. All the above materials were used as received without further purification.

B. Synthesis

The UV-curable waterborne polyurethane acrylate (UV-WPUA) was prepared according to the schematic outline as shown in Scheme 1.



Scheme 1 Synthesis route of the UV-WPUA resin

A four-necked round bottom flask was equipped with a mechanical stirrer, a thermometer, and a condenser with drying tube. First, TDI was added into the flask with N_2 protection. Then stoichiometric PEG600 was slowly dropped in the above reaction vessel by dropping funnel and stirred at $80\sim 90^\circ\text{C}$ for 2~3 hrs. Second, the reactor vessel was cooled down below 60°C , BD and DMPA were slowly added in the above reaction vessel *via* dropping funnel and stirred at $70\sim 80^\circ\text{C}$ for 2~3 hrs. The reactor vessel was again cooled down to 50°C or lower. TEMPO was then added as an inhibitor for the 3.0 wt.% of unsaturated double bonds of the acrylate, HEMA was drop wise added into the above reaction vessel under stirring; reaction temperature was controlled at $60\sim 70^\circ\text{C}$ for 2~3 hrs to form the UV-WPUA prepolymer. In order to control the viscosity of the reaction, the suitable amount of acetone was added as a diluent during the reaction. Finally, the reaction was completed by adding TEA to neutralize the residual carboxylic groups in the resin over a period of 30 min under vigorous stirring. Chain extension continued until -NCO peak (2273 cm^{-1}) in the FTIR spectrum had completely disappeared and the unsaturated double bonds ($-\text{CH}=\text{CH}_2$) peak (1600 cm^{-1}) had emerged as shown in Fig. 1.

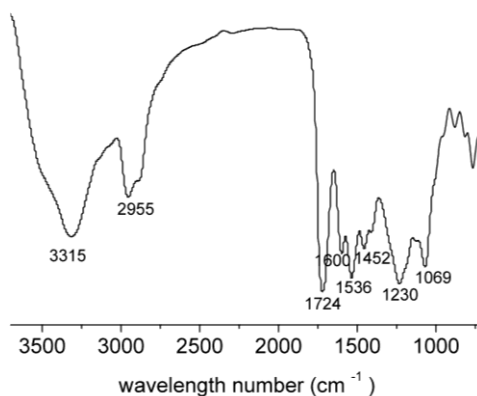


Fig. 1 FTIR spectrum of the UV-WPUA resin

The polyurethane acrylate resin was obtained by evaporating acetone, resulting in a light yellowness viscous liquid (79% solid content). The reactive conditions were optimized by the orthogonal experiment, such as -COOH content, PEG molecular weight, order of reagent addition, type of neutralization agent and neutralizing degree, type of inhibitor and its water-solubility. Influence of initiator's content, dry time and dry temperature, and the UV-curing rate were investigated. The bulk property of the resin was characterized.

C. The Orthogonal Experiment of the Optimizing Formulation

According to the demands of the basecoats on the surface of the paper packaging such as wine bottle label, plating-aluminum card, and cigarette case, the optimizing formulation was performed by the orthogonal experiment. The properties of the product included water solubility, rate of UV-curing and flexibility of film. They are corresponding influenced

by content of carboxyl group (-COOH), content of unsaturated double bonds (-CH=CH₂) and the molecular weight of PEG. The important three factors such as the molecular weight of PEG (signal as A), and the content of carboxyl group (-COOH) (signal as B) and the content of unsaturated double bonds (-CH=CH₂) (signal as C), was designed by L₉(3³) orthogonal list with three factors and 3 level such as in Tables 1 and 2.

TABLE 1 FACTORS OF THE ORTHOGONAL

factor level	A \overline{M}_n of PEG	B -COOH %	C -CH=CH ₂ %
1	A ₁ = 400	B ₁ = 1 %	C ₁ = 1 %
2	A ₂ = 600	B ₂ = 3 %	C ₂ = 3 %
3	A ₃ = 1000	B ₃ = 5 %	C ₃ = 5 %

TABLE 2 ORTHOGONAL EXPERIMENTAL DESIGN

factor number	A \overline{M}_n of PEG	B -COOH %	C -CH=CH ₂ %
1	A ₁	B ₁	C ₂
2	A ₁	B ₂	C ₃
3	A ₁	B ₃	C ₁
4	A ₂	B ₁	C ₃
5	A ₂	B ₂	C ₁
6	A ₂	B ₃	C ₂
7	A ₃	B ₁	C ₁
8	A ₃	B ₂	C ₂
9	A ₃	B ₃	C ₃

D. Characterization of UV-WPUA Resin

The Infrared spectra were recorded on an MAGNA-IR750 (Nicolet Instrument Corporation, USA). The particle ratio of the resin emulsion was measured by microtrac particle size analyzer (Malvern II C, He-Ne type laser with wavelength 633 nm was used) the range of particle size is 0.5~1000 nm. The viscosity of the product was determined with an NDJ-1 model spinning viscometer (Balance Instrument Co., China) with the speed of 750 rpm. The solubility of the resin in water was investigated by different concentration of 60%, 40%, 20%, 10% and 1% in water at ambient temperature. If the solution is clear, the water solubility of the resin is good. The density of the resin was measured by the gravity bottle with the accuracy of 0.001. The VOC (volatile organic compounds) of the resin was measured by gas chromatography according to the International Standard ISO 2884-2-2003. The solid content of the resin was obtained by evaporating acetone according to the International Standard ISO 3251-2003. Other properties of the resin were also measured according to the International Standard respectively.

E. Preparation of UV Curable Samples and UV-Curing

The formulations of all UV-curable samples were prepared by adding 5.0 wt.% of Darocur2959 as an initiator to the above solution of the UV-WPUA resin, then adding water into the solution to dilute the solid content to 60% from 79%. All samples were coated on the surface of the write card paper (Unite, DB, 225 g/m²) by plate coater or the coil painter with 3~5 μm thickness at room temperature. First, all samples were heated to 80~90 °C for 2 hrs to remove the water, then UV-curing on a UV conveyor system with a 2400 W high pressure mercury lamp at the transmit rate of 627 cm/min. Curing time was measured by the finger-press method.

III. RESULTS AND DISCUSSION

A. Bulk Property of the UV-WPUA Resin

Bulk properties of the UV-WPUA resin were measured as shown in Table 3.

It could be seen that the bulk properties of the resin is excellent with good appearance, high solid content, good water solubility and long stability of storage more than 6 months. Reaction condition and synthetic formulation of the resin very much determined the coating performance. Content of -COOH, and molecular weight of PEG were confirmed by orthogonal experiment. The theoretical optimized result in Table 4 is A₂B₃C₃ which depends on the total scope (equal to Y_i) summing up by the important three factors such as molecular weight of PEG (A_i), and content of carboxyl group (-COOH) (B_i) and the content of unsaturated double bonds (-CH=CH₂) (C_i), where Y_{ji} is the average value of Y_i to evaluate bulk performance of UV-cured film, and R_j is the grade differential to the average value of Y_i .

TABLE 3 BULK PROPERTIES OF THE UV-WPUA RESIN

Property	Criteria	Results	Test method
Appearance	Clear and no mechanical impurity	Light yellowness, Clear and no mechanical impurity	Visualization
Solid content (%)	> 75%	79.0	ISO 3251-2003
pH value	6.0~8.0	7.0	Fine pH paper
Density (g/mL)	1.1~1.3	1.15	ISO 2811-1974
Viscosity (mPa s)	< 6000	16366	ISO 2884-2-2003
Solubility of water	Good water soluble no turbid phenomenon	Miscibility with water in any ratio	Q/STDN2-2006
Stability of storage	> 6 months	> 6 months	Q/STDN2-2006

TABLE 4 DESIGN AND EVALUATION OF THE ORTHOGONAL EXPERIMENTAL

No.	A	B	C	Water solubility	Flexibility	Rate of UV-curing	y_i
1	A ₁	B ₁	C ₂	7.0	15.0	21.0	43.0
2	A ₁	B ₂	C ₃	17.5	15.0	35.0	67.5
3	A ₁	B ₃	C ₁	21.0	15.0	7.0	43.0
4	A ₂	B ₁	C ₃	24.5	22.5	35.0	82.0
5	A ₂	B ₂	C ₁	31.5	22.5	14.0	68.0
6	A ₂	B ₃	C ₂	35.0	30.0	35.0	100.0
7	A ₃	B ₁	C ₁	35.0	28.0	7.0	70.0
8	A ₃	B ₂	C ₂	35.0	30.0	14.0	79.0
9	A ₃	B ₃	C ₃	35.0	30.0	35.0	100.0
y_{j1}	153.5	195.0	181.0	$\sum_{i=1}^9 y_i = 652.5$			
y_{j2}	250.0	214.5	222.0				
y_{j3}	249.0	243.0	249.5				
\bar{y}_{j1}	51.2	65.0	60.3				
\bar{y}_{j2}	83.3	71.5	74.0				
\bar{y}_{j3}	83.0	81.0	83.2				
R _j	32.1	16.0	22.9				
optimum level	A ₂ B ₃ C ₃			Optimum result is A ₂ B ₃ C ₃			
key factor	A C B						

From Table 4 it shows that A is the prior factor, the second is C, and then B. As B factor which determines the water solubility, it is white powder; it can lead to the viscosity of the reaction system increasing quickly and get out of hand. What's more, its monomer cost is high. When the content of -COOH is 1.0 wt.%, the water solubility of the resin is bad, and then the content of -COOH is 3.0 wt.% or 5.0 wt.%, the water solubility of the resin is good and makes little differences. Therefore, it's suitable to choose B when the content of -COOH is 3.0 wt.% in practical production. For the same reason, to balance the cost and the properties of the resin, the experimenters choose C when the content of unsaturated double bonds (-CH=CH₂) is 3.0 wt.%, choose A when the molecular weight of PEG is 600, the rate of UV-curing and flexibility can reach the company's technical demand.

As a whole, given the cost and practical production, the optimized result is A₂B₃C₂.

Table 5 showed the comparative analysis of A₂B₃C₃ and A₂B₂C₂, taking into consideration the cost and synthetic process, the results of the orthogonal optimization indicated that the synthetic resin had excellent property when the content of carboxyl group (-COOH) was 3.0 wt.%, the content of unsaturated double bonds (-CH=CH₂) was 3.0 wt.%, and molecular weight of PEG was 600.

TABLE 5 COMPARATIVE ANALYSIS OF A₂B₃C₃ AND A₂B₂C₂ IN RESULT

No.	Water solubility	Flexibility	Rate of UV-curing
A ₂ B ₃ C ₃	Miscibility with water in any ratio	Folding times n > 100	UV-curing completely in one time
A ₂ B ₂ C ₂	Miscibility with water in any ratio	Folding times n > 100	UV-curing completely in one time

B. FTIR Spectrum Analysis of the UV-WPUA Resin

The structure of the UV-WPUA was confirmed by FTIR spectroscopy as shown in Fig. 1. It showed that the absorption peaks of typical polyurethane at 3315~3350 cm⁻¹ (N-H, hydrogen bond), 2800~2955 cm⁻¹ (-CH₃ and -CH₂-), 1724 cm⁻¹ (C=O), respectively.

C. The Particle Ratio of the UV-WPUA Resin

The particle ratio of the UV-WPUA resin emulsion was measured by microtrac particle size analyzer. The size distribution and statistics graph by the volume was shown in Figs. 2 and 3.

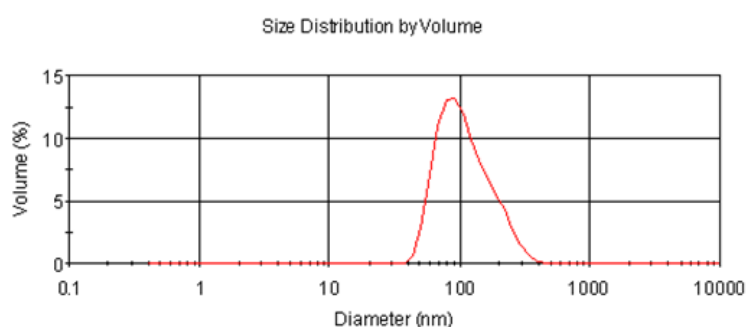


Fig. 2 Size distribution of the particle diameter in the resin emulsion by volume

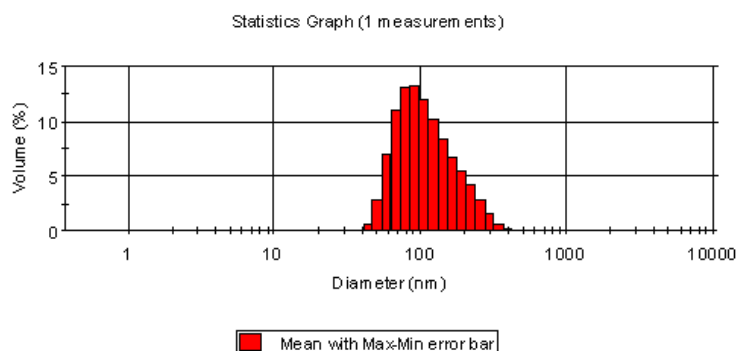


Fig. 3 Statistic distribution of the particle diameter in the resin emulsion by volume

The result shows that z-Average size of the particle diameter in the resin emulsion is 123.1 nm, the index of size distribution (polydispersity) is 0.117. Generally, the size of the particle is smaller, the stability of the emulsion is longer, and then the water solubility of the resin is better. Diluting the resin with water, the result shows that the resin can be miscible with water in any ratio and has no turbid phenomenon.

D. Water Soluble Character and Stability

Water solubility of the UV-WPUA resin was measured by adding different content of water and the mixture of water and ethanol (70:30) to dilute the solid content of the resin from 100% to 79.4%, 68.2%, 62.3%, 53.3%, 43.3%, 35.4% and 83.6%, 67.0%, 57.0%, 49.0%, 45.0%, respectively. The viscosity and the water solubility of the UV-curable coatings were as shown in Tables 6 and 7.

TABLE 6 APPEARANCE, SOLID CONTENT AND VISCOSITY OF THE RESIN BY USING WATER AS A DILUENT

Solid content (%)	79.4	68.2	62.3	53.3	43.3	35.4
Viscosity (mPa s)	16366	11334	6500	4666	950	536
Appearance	clear	clear	clear	clear	clear	clear

TABLE 7 APPEARANCE, SOLID CONTENT AND VISCOSITY OF THE RESIN BY USING THE MIXTURE OF WATER AND ETHANOL AS A DILUENT

Solid content (%)	83.6	67.0	57.0	49.0	45.0
Viscosity (mPa s)	30541	2406	533	200	97
Appearance	clear	clear	clear	clear	clear

Fig. 4 shows the influence of different diluent to viscosity of the UV-curable coatings. The results show that the water solubility of the UV-WPUA resin is excellent, and the appearance of the aqueous system is clear during the diluting process. The viscosity of the resin decreased with the solid content decreasing. The mixture of water and ethanol (70:30) is more effective than water as a diluent alone.

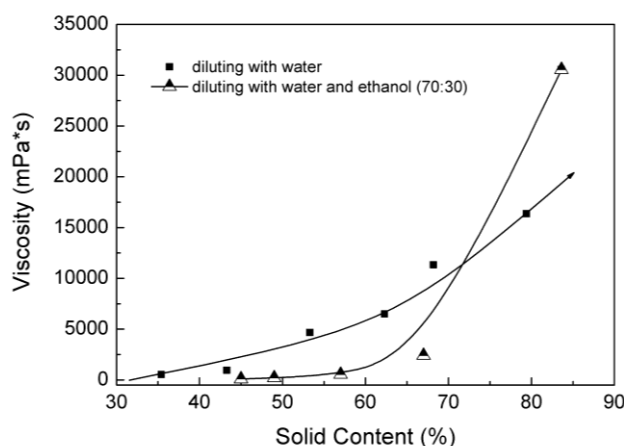


Fig. 4 Influence of solid content on the viscosity of UV-WPUA resin

When the TEA (triethanol amine) was used as a neutralizer, the water-solubility of the resin was excellent. TEA was a good neutralizer since its UV-cured coating could easily absorb water when it is cured. Ammonia was a bad neutralizer, because the water-solubility of the resin was low. With the increase of hydrophilic groups and neutralization degree, the water-solubility and storage stability of the resin increased; with the increased inhibitor level, the storage stability improved. When inhibitor level reached 0.03 wt.%, The emulsion can be stable for more than six months.

E. The Performance of the UV-curing Coatings

Bulk performance of the UV-curing coatings was measured shown in Table 8.

TABLE 8 BULK PERFORMANCE OF THE UV-CURING COATINGS

Targeted Performance	Results	Test Methods
Surface tension ≥ 39 mN/m	41 mN/m	Q/STDN1-2005
Good adhesion on paper	pass	3M adhesive tape
Good adhesion on aluminum film	pass	3M adhesive tape
Right folding (90°) ≥ 20 cycles	≥ 30	Q/STDN1-2005
Back folding (180°) ≥ 1 cycle	≥ 10	Q/STDN1-2005
Gloss (20°) ≥ 30	30.5	Q/STDN1-2005
VOC content ≤ 200 ng/m ²	131.7 ng/m ²	Gas Chromatography

The results show that surface tension is 41 mN/m, higher than targeted 39 mN/m. Adhesion on the card paper and aluminum is good. The flexibility is excellent, 90° right folding (30 cycles) and 180° back folding (10 cycles) well passes required 20 and 1 cycles, respectively. VOC content is 131.7 ng/m², less than the targeted 200 ng/m² by Gas Chromatography. The photography of the UV-curing coatings on paper package was shown as in Fig. 5. It clearly indicates that the UV-curing coatings have a good appearance, a higher gloss, and are suitable for protecting printed surface.



Fig. 5 Paper coated with the UV-WPUA coating

IV. CONCLUSIONS

A novel waterborne UV-curing polyurethane acrylate (UV-WPUA) resin was prepared. The content of -COOH , the molecular weight of PEG and the content of unsaturated double bonds (-CH=CH_2) were confirmed by orthogonal experiment. The results indicated that the synthetic resin had excellent performance when the content of carboxyl group (-COOH) was 3.0 wt.%, the content of unsaturated double bonds (-CH=CH_2) was 3.0 wt.%, and the molecular weight of PEG was 600.

The optimal condition, such as type of neutralizer, type of inhibitor and water-solubility were performed. The results show that the optimal condition to synthesis the UV-WPUA resin is as follows: the reaction temperature is 80~90 °C, and the temperature of feeding raw material is below 50 °C, and reaction time of every step is 2~3 hrs. Feeding order of raw material is first, TDI was added into the flask, and then PEG600 was slowly dropped. Secondly, BD and DMPA were slowly added. Thirdly, HEMA with TEMPO (0.03 wt.%) was added. Fourthly, the reaction was completed by adding TEA to neutralize the residual carboxylic groups. Finally, the resin emulsion was formed under vigorous stirring by adding the suitable water or the mixture of water with ethanol over a period of 30 minutes.

The optimal conditions for UV-curing process of the UV-WPUA resin such as the influences of initiator's content, dry time, dry temperature, and inhibitor's content on UV-curing rate were discussed. The formulations of all UV curable samples is 5.0 wt.% of Darocur 2959 as an initiator, the solid content of the resin is about 60%, the thickness of UV-curable coating was controlled to 3~5 μm . All samples coated were heated to 80~90 °C for 2 hrs to remove the water before curing, it is a special technique necessary for waterborne UV-curable coatings.

The bulk performance of UV-curing coatings of the UV-WPUA resin was appraised. Flexibility, adhesion, and brightness of the UV-cured coatings were excellent. UV-curing coatings of the UV-WPUA resin were successfully applied to the card paper applied to the packaging materials such as wine bottle label, the plating-aluminum card, and the cigarette case. It is clear that waterborne UV-curing coatings have a potential for various applications.

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He and co-workers have studied on the reaction kinetics of controlled/living photo-induced polymerization of (meth)acrylate and styrene monomers in bulk, solution and emulsion. They have developed a new route of photo-induced controlled/"living" free radical polymerization at ambient temperature and systematically researched the reaction kinetics of controlled/"living" photopolymerization of reactive Hindered Amine Piperidinyl Derivatives(r-HAPD). Many research papers have been published on the academic journals for polymer science, such as a *J Polym Sci, Part A, Polym Chem*, and *J Membr Sci*. Some papers are listed as follows:

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The photo-curing technology has found a growing number of applications mainly in the coating industry, graphic arts, and microelectronics, replacing conventional thermally cured solvent-based coatings and adhesives in recent years. They have developed UV-curable film of the transfer printing, UV-curing resin of the vacuum metallization on the surface of plastics, and special developed the water-borne polyurethane-acrylate (PUA) and application to UV-curing coatings on the package of paper and on the glass substrates, 8 patents have been authorized.

Prof. Liu's memberships are listed as followed:

1. International Membership of RadTech North USA
2. Academic membership of RadTech China
3. International Membership of RSC, Advancing the Chemical Sciences, UK
4. Technological Adviser for Polymer Industry Association of Shenzhen, China