

## Status and progress of RadTech in China

Hong Xiaoyin<sup>1&2\*</sup>, Jin Youkai<sup>2</sup>, Jin Yangzhi<sup>2</sup>

<sup>1</sup> Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Chemistry Department, Tsinghua University, <sup>2</sup>RadTech China

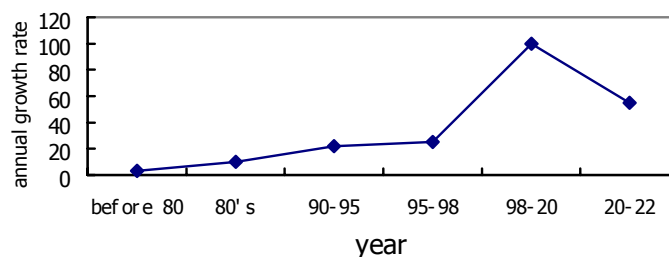
\*Beijing, 100084, China

Fax:86-10-62771149, Email: [hongxy@mail.tsinghua.edu.cn](mailto:hongxy@mail.tsinghua.edu.cn)

### 1. Introduction: High Growth Rate

Since 1993 the market of RadTech in China has developed significantly. During this period companies have rapidly expanded their market. In spite of the negative influence of Asia financial crisis and 9.11 event, the annual growth rate of consumption of UV curable resins in China is more than 25%. Since 1998 output of products associated with RadTech has been growing at an even higher rate. The total production of raw materials almost doubled from 1998 to 2000. In addition, from 2000 to 2002 the annual growth rate kept above 50%. Figure 1 shows the increase of annual growth rate of RadTech products (consumption) in China during 1980 to 2002. China's entrance to WTO in 2002, the 2008 Olympic Game and the government's encouragement to companies to produce green products provide even brighter opportunities for further development of RadTech in China.

Fig. 1 annual growth rate



### 2. Markets and Production of Raw materials

Although most of oligomers, monomers, and initiators were imported before 1998, the production of those materials in China increased rapidly in recent years. Photoinitiators and monomers started to export from 2001. Figure 2 shows the growth of production of main raw materials in China. Figure 3 and 4 show the increase in export.

Fig. 2 Growth of raw materials

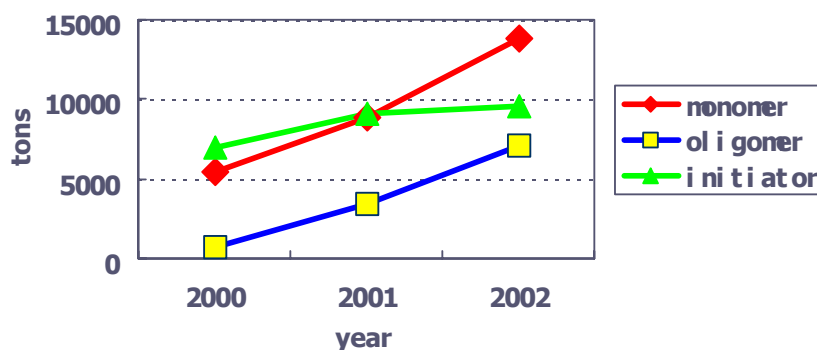
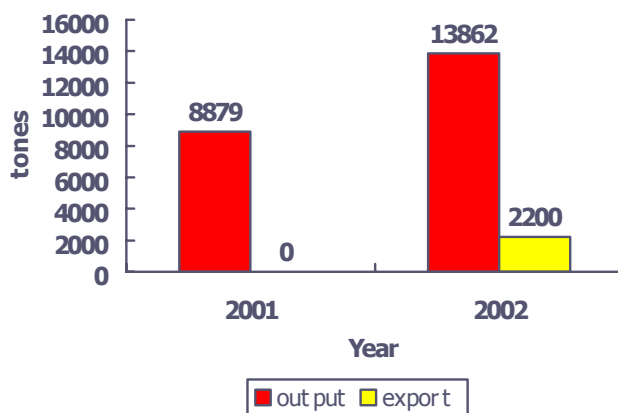


Fig. 3 Output and export of Initiators



Fig. 4 Output and export of monomers



Now Chinese manufacturers can produce not only the common kinds of photoinitiators such as 1173, 184, 651, but also special initiators (Table 1).

Table 1 Initiators produced in China in 2002

Photoinitiators	Annual Tonnage
Benzophenone	2760
2,2'-Dimethoxy-2-phenylacetophenone (651)	1600
2-Hydroxy-2-methyl-1-phenylpropan-1-one (1173)	2260
1-Hydroxycyclohexyl phenyl ketone (184)	1140
2-Methyl-1-(4-[methylthio]phenyl)-2-(4-morpholinyl)-1-propanone (907)	860
Isopropyl thioxanthone (ITX)	500
TPO	2400
Special Initiators	160

Multi-functional monomers produced in China for UV curable resins are TMPTA, PETA, DEGDA, TEGDA, PDDA and NPGDA (Table 2). Monomers such as TPGDA, POGTA, EOTMPTA,

PONPGDA and others are in development. The annual output of domestic product of oligomers is shown in Table 3. Although significant improvement has been made in the past years, current production cannot meet the need of domestic market. As a result, most oligomers are still imported. Currently, many companies are making efforts to improve the quality of their products and investing on producing new oligomers. A monomer plant was built by UCB in Shanghai in 2000, which promotes the production of monomers and oligomers in China.

Table 2. Main monomers produced in China in 2002

Monomers	Annual Tonnage
TMPTA	4130
TPGDA	4450
NPGDA	370
HDDA	1050
PDDA	110
PETA	20
DPGDA	232
BDDA	15
EO-TMPTA	505
PO-NPGDA	160
HEMA	2500
TMPTMA	10
Others	310

Table 3. Main Oligomers produced in China in 2002

Oligomers	Annual Tonnage
Epoxy Acrylates	3320
Modified Epoxy Acrylates	1780
Urethaneacrylates	1737
Others	3922

### 3. Market and production of End use products

#### 1. UV curable coating and ink:

Coatings and inks are the main application of UV curable resins(Figure 5). The total consumption of radiation curable coatings and inks were ca. 18740 tons in 2002. Table 4 shows the main application of UV curable coating in 2002. The major market of UV curable coating is for flooring, especially for wood, bamboo and PVC floorings. Overprints for paper are another important market. The market of UV curable coatings used for anticorrosive coating, metal coating, automotive coating also grows rapidly.

Fig 5. Growth of production of ink and coatings

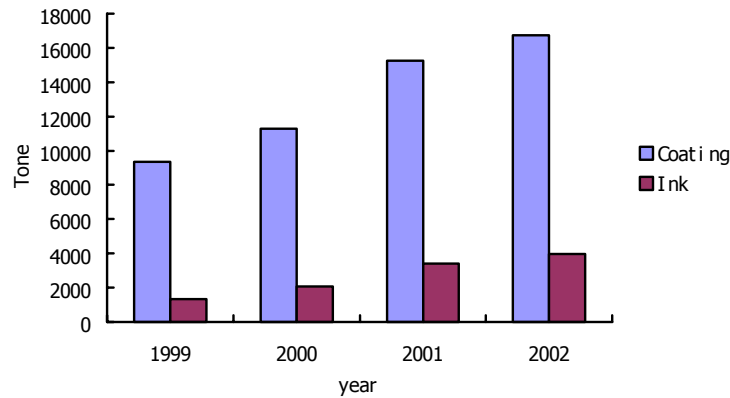


Table 4. The Application of UV curable Coatings in China in 2002

Application	Annual Tonnage
Flooring Coatings	
Wood & Bamboo	8955
PVC	1456
Overprints for paper	4462
Plastic Coatings	908
Automotive Coatings	380
Metal Coatings	80
Appliance	50

Table 5. Application of UV inks in 2002

Application	Annual Tonnage
Offset Inks	232
Flexographic Inks	142
Screen Print Inks	1415
Optical Disk Inks	450
PCB	1324
PCB photoimaging	405

In 2002 the total output of UV curable inks is ca. 3968 tons. The main applications are shown in table 5.

### 3. Printing plate

Offset PS plates still are one of the fastest developing products in China. Since 1990 the output of PS was doubled per one or one and half years, the capacity of production in 2001 was ca. 100 million m<sup>2</sup> and output is ca. 60 million m<sup>2</sup> respectively, and about 1/4 of product was exported to East-South Asia, Africa and Europe. The output of solid photopolymer plate was more than 100,000 m<sup>2</sup>. The consumption of liquid photopolymers relief plates was 50,000 -100,000 m<sup>2</sup>. The consumption of Flexo plates was more than 50,000m<sup>2</sup>, among which half was imported. The growth of these last three products is rather low.

#### 4. Some aspects of R & D in China

Some remarkable progress of research and development has been achieved in recent years. The following is a summary of some aspects of recent achievements

##### 1. Photo induced self assembly of ultra thin film and its application

A novel phenomenon related with darzo resin was discovered by W.X. Cao. Using Diazo resin as the cationic polyelectrolyte and poly (sodium styrenesulfanate) as anionic polyelectrolyte, a polyelectrolyte complex containing diazonium group (PEC-N<sub>2</sub>) was made. This complex is insoluble in water and organic solvents because of the ionic crosslinking structure, but is able to dissolve in ternary mixture such as H<sub>2</sub>O-DMF-LiCl. After exposure to UV light, PEC-N<sub>2</sub> turns to covalent structure from ionic structure and becomes insoluble in any solvents (Scheme 1). The photoinduced reaction of polyelectronic complex can be used for developing an image transfer process with or without development. The ternary solvents could be used as developer for development. Based on the discovery, self assembled mono or ultra film multilayer films were fabricated (Shown in Fig 5) and were used as photoresist for negative pre-sensitized printing plate. The ultra-thin (20-30 nm) negative presensitized printing plates have excellent durability and ink-stain behaviors. The pressrun of the ultra-thin PS plate is more than 7x10<sup>4</sup>.

Scheme 1. The Reaction of polyelectrolyte complex containing diazonium group

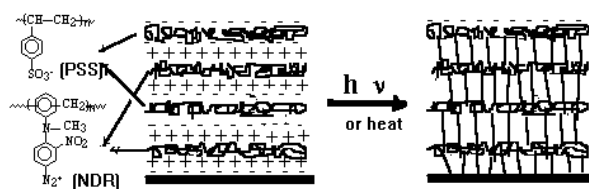
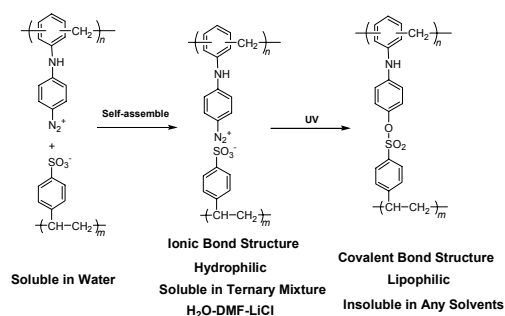


Fig.5. The Mechanism of formation of self assembled multilayer

##### 2. Photo-initiated crosslinking of polyethylene

It was difficult to crosslink thick solid samples of PE homogeneously because of two main problems: poor penetration of UV light in bulk PE and slow reaction rate of photocrosslinking of PE. The major problems in photocrosslinking of PE in bulk have been overcome by B.J.Qu, the depth of PE homogeneous photocrosslinking is increased to at least 5mm to meet the requirement of 10 KV XLPE cables.

A photocrosslinking process for polyethylene and its industrial irradiation apparatus were developed and applied successfully to the manufacture of thin wall crosslinked high voltage

television XLPE wires and power cables. A block diagram of commercial process of photocrosslinked polyethylene wires and cables is shown in Figure 6. The photocrosslinked XLPE-insulated high voltage wires produced by this new technique possess excellent electrical and mechanical properties and much lower operating cost compared with electron beam crosslinking technique. The homogeneous photocrosslinking of PE bulk with thin colored coating to produce colorful cables recently was realized

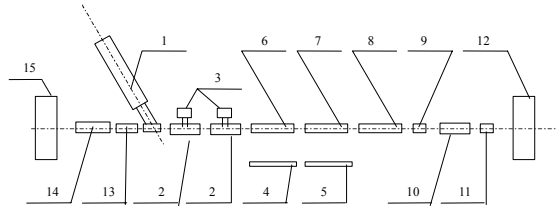
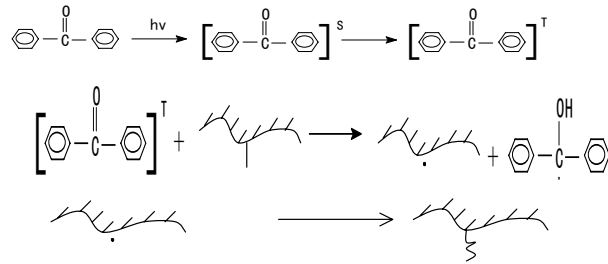


Fig. 6. Block diagram of production line of photocrosslinked XLPE wires and cables.

1. Extruder; 2. UV irradiation unit; 3. exhaust fan; 4. cabinet of electric controller; 5. cabinet of electrical system; 6. hot water tank; 7. warm water tank; 8. cool water tank; 9. length counter; 10. down-drawing; 11. test machine of breakdown; 12. take up; 13. preheater; 14. up-drawing; 15. pay-off.

### 3. Photo induced surface photografting

W. T. Yang et al have conducted researches on surface photografting polymerization for modification of polymer films. With simple photografting approach, the surface contact angle to water of Teflon could be greatly reduced and its adhesion strength to epoxy resin could increase about one hundred times. The principle is shown in scheme 2.



Scheme 2. Principle of surface photo grafting Polymerization

Based on the principle, some very effective continuous surface modification methods for polymer films, fibers and articles have been developed. Some breakthroughs for practical applications were achieved. The modified films of LDPE, PVC and BOPET are used as greenhouse film with excellent antifogging properties. With this process the printing property of PP plastic films is greatly improved.

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