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Systemic research of Fluorescent Emulsion Systems and its polymerization process with fluorescent probe by AIE mechanism

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Abstract: In this paper, AIE luminogen, which was used as a fluorescent probe, was synthesized and copolymerized with acrylate monomers to study the process of emulsion polymerization and the properties of fluorescent emulsion. At first, according to the changes in fluorescence spectra, emulsion polymerization process can be marked with real-time monitoring. Then, by varying the relative content of AIE luminogen, glass transition temperature of the synthesized emulsion, the size of the emulsion particle, the content of emulsion, and the detection temperature, etc. the interaction between fluorescence properties and the intrinsic properties of the emulsion were studied systematically. It should point out that the microscopic motion of the segment of polymer can be studied by Fluorescence spectra with the help of fluorescent probe. Traditionally, AIE luminogens are applied in optoelectronics and biological domains at the state of small organic molecules. When AIE luminogen is connected with polymer chains by chemical bond, a lot of interesting phenomenon can be found. The research results not only provide a new method to study emulsion polymerization process and the properties of emulsion, but also the synthesized emulsion with the properties of fluorescence may broaden the application of AIE mechanism.

Key Words: emulsion polymerization; fluorescent acrylate emulsion; aggregation-induced emission; fluorescence spectrum; glass transition temperature

Introduction

Polymer particles have attracted a great deal of interest and have been utilized in a wide range of fields[1]. Waterborne polymer colloids, often referred to as 'emulsion dispersions', are well-established for diverse applications in many commercial products from different industrial segments including cosmetics, pharmaceuticals, adhesives, coatings and paints[2-5]. A key advantage of the colloidal approach is that it enables direct control of internal structure organization of the particles at nanoscale[6]. Nanostructured lattices have been commonly prepared by emulsion polymerization processes in the presence of emulsifying agents to ensure the physical stability and the nanometric size of the resultant particles. Examples of

miniemulsion, suspension or dispersion polymerization processes can be found in the literature but emulsion polymerization is by far the most frequently used technique [7]. TraditionAE methods to study emulsion and emulsion polymerization process including FTIR, ^{1}H NMR or ^{13}C NMR, DSC, TGA, TEM, SEM, and Laser Diffraction Particle Size Analyzer to study their chemical substance, their structure, morphologies, and thermodynamic performance[1,7]. However, as the multiphase system, a lot of research conclusion about it is still obscure, and it still need to carry on further investigation to research the properties of emulsion and systematacially.

Beside studying the intrinsic properties of the emulsion, the functionalization of emulsion particles is also the important research work. When fluorescent molecule were incorporated into the emulsion particles, they attracted increasing interest owing to their potential applications ranging from optoelectronics to biological imaging and disease therapy[8]. Incorporation of polymerizable organic dyes including uoresceins, rhodamines, 1,8-naphthalimides, diverse aromatic dyes, coumarins, azo-dyes and oxadiazoles into polymers using polymerization methods including free radical polymerization, reversible addition-fragmentation transfer polymerization, atom transfer radical polymerization, nitroxide mediated polymerization and emulsion polymerization etc. have been reported[8]. However, these fluorescent organic particle based on conventional organic dyes often lead to a significant decrease of their fluorescent intensity after their self-assembly into nanoparticles because of the notorious aggregation-caused quenching effect[9,10].

In 2001, a novel phenomenon of aggregation-induced emission(AIE) was first found by Tang's group from propeller-like siloles, whose emission was very weak in solution but became intense as aggregates formed[11]. Such abnormal emission behavior has drawn great research interest, for it is exactly opposite to the common belief that the emission of chromophores decreases in the aggregate state[12-14]. This intriguing finding paves a new avenue to tackle the notorious ACQ of conventional chromophores. Bin Liu and Ben zhong Tang *et al* synthesized TPE-TPA-DCM, fabricated its BSA nanoparticles, and explored their in vivo and in vitro bioimaging

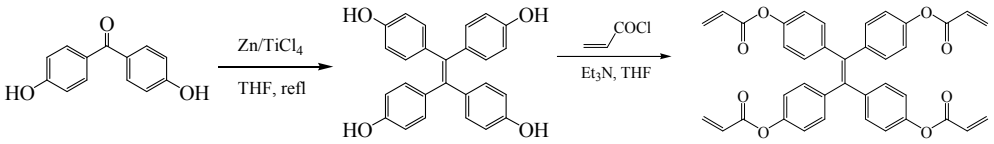
applications. The TPE-TPA-DCM possesses both TICT and AIE features, and its BSA-formulated NPs show efficient FR/NIR fluorescence with low cytotoxicity, uniform size and spherical morphology[15]. Xiaoyong Zhang, Yen Wei *et al* obtained polymer nanoparticles (named as PhE–Pst NPs) exhibited strong fluorescence and high water dispersibility owing to the partial aggregation of PhE and the surface covered with a hydrophilic shell. More importantly, these FONs showed spherical morphology, uniform size (about 200 nm) and excellent biocompatibility, making them promising for bioimaging applications[16]. Tang *et al* reported highly emissive AIE-based inorganic-organic nanoparticles with core–shell structures which were fabricated by a one-pot, surfactant-free hybridization process. The resultant FSNPs were mono dispersed with smooth surfaces. They possessed high surface charges, AIE features and excellent colloidal stability. Furthermore, the particle diameters and emission efficiencies of the FNPs could be manipuiable by changing the reaction conditions and luminogen loadings[17,18].

Although fluorescent organic particles had been studied for a long time and showed great prospects in application, the relationship between their fluorescent property and other intrinsic properties still need to be researched carefully. In this paper, tetraphenylethene-containing tetra-acrylates was synthesized and used as a fluorescent probe to carry on the systematic research work. Tetraphenylethene (TPE), as one of the typical fluorescent molecule with AIE character, is found to be non-emissive in dilute solutions but became highly luminescent when their molecules are aggregated in concentrated solutions or cast in solid films[19]. In detail, in a dilute solution, TPE undergoes dynamic intramolecular rotations against its double bound and renders its molecule non-luminescent. On the other hand, in the aggregate state, the molecules cannot pack through a π-π stacking process due to its propeller shape, while the intramolecular rotations of its aryl rotors are greatly restricted owing to the physical constraint. This restriction blocks the non-radiative pathway and opens up the radiative channel[20-21].Taking the advantage of its unique properties, the fluorescence intensity of the polymer modified with TPE-containing tetra-acrylate can

be efficiently enhanced by increasing its concentration, loading without the need to avoid the aggregation of the probes. It is possible to study the emulsion polymerization process and the properties of emulsion through fluorescence spectrum by taking advantage of AIE mechanism.

Results and discussion

Tetraphenylethene-containing tetra-acrylates was synthesized according to the previous document[22]. Briefly, McMurry coupling reaction of 4,4'-diydroxybenzophenone catalyzed by $TiCl_4$-Zn in THF generated intermedate tetrahydroxy tetraphenylethene. Since it readily underwent oxidation reaction in air, they were treated with acryloyl once isolated to furnish the product, TPE-containing tetra-acrylate. White solid; overall yield 38%. Detail structural analysises are provided in the Fig.1S.



Scheme 1 Synthesis of TPE-containing tetra-acrylate

The standard emulsion polymerization process was carried on as follows. The synthesized TPE-containing tetra-acrylate was blended with acrylate monomers and prepared fluorescent acrylate emulsion *via* emulsion polymerization with sodium dodecyl sulfate(SDS) as the emulsifying agent and potassium persulfate (KPS) as the thermal initiator. In brief, acrylate monomers mixed with AIE luminogen were dispersed in water, which contained a minute amount of the emulsifying agent and thermal initiator. After the blending mixtures were emulsified with intense mixing, the polymerization was carried out at 80℃ for 10h with continuous stirring. Different conditions were set to study the interaction between fluorescence properties and the other intrinsic properties of the emulsion, such as the relative content of AIE luminogen, the size and the content of fluorescent acrylate emulsion, the glass transition temperature of the polymers, and the detection temperature. To identify the samples accurately, the prepared different fluorescent acrylate emulsions are named from AE-TPE-A to AE-TPE-R. Detailed contents of the preparation process are

presented in the supporting materials.

At first, sample AE-TPE-D was selected as the example to study emulsion polymerization process, which is presented in Fig.1. During the process of polymerization, AIE luminogen acted as the probe to tracking the whole reaction process according to fluorescence spectrum. Owing to the electronic transition of the TPE unit, the absorption spectra of TPE-containing tetra-acrylate and fluorescent acrylate emulsion exhibited the absorption peak at around 460nm.

---------- Fig.1 ----------

Fig.1(a) Fluorescence spectra of ongoing reacting fluorescent acrylate emulsion; (b) Wavelength and intensity of PL spectra of ongoing reacting fluorescent acrylate emulsion and (c) Pictures of ongoing reacting fluorescent acrylate emulsion taken by camera varied with reaction time (From 5 to 600min)

At first, no obvious polymerization phenomenon happened before 50min according to the pictures taken from camera and the results of fluorescence spectra. During this stage, AIE luminogen was just physical dispersed into micelles with methylmethacrylate monomer, and thermal initiators started to decompose and generate free radicals in water. The fluorescence spectra of AIE luminogen showed a distinct emission peak at around 485nm because of the poor solvent system. However, with the reaction carrying on, autoacceleration effect[23] happened from 55min due to higher concentration of monomers and free radicals in the micelles. The peak position red shifted to 455nm and the intensity enhanced for about fourteen times. We have proposed that restriction of intramolecular rotation (RIR) is the main cause for the AIE phenomenon [24]. When AIE luminogen and monomers are knitted together by covalent bonds to form polymer chains, the RIR process will partially activate. This restriction blocks the non-radiative pathway and opens up the radiative channel[25], and thus make the synthesized acrylate emulsion somewhat emissive. From 55min to 120min, in the second process of polymerization, more intramolecular rotation of AIE luminogen was restricted due to more of it had reacted and formed the polymer chains. According to AIE mechanism, the fluorescence intensity increased with the content of the reacted AIE luminogens. So in this stage, fluorescence intensity of the reacting

system increased with the time. With the reaction continued, the fluorescence intensity of the reaction system maintained a relatively stable state from 120min to 300min. It meant that AIE luminogens had been ran out of during the third stage. However, due to metastable nature of acrylate emulsion, it might collide, aggregate and deposit at high temperature. So, with the reaction preceded, a part of fluorescent acrylate emulsion formed gel and precipitated, and the fluorescence intensity decreased with reacting time.

To verify the results of fluorescence spectra, GPC and solid content of the emulsion measurements were carried on. As can be seen from the supporting materials, the results of them confirm the result fluorescence spectra. Typical process of emulsion polymerization can be summarized as follows: In the beginning, the reactive monomers were wrapped in the micelles formed by emulsifying agent and dispersed in water. At this stage, the content of the free radicals was quite low, and the reaction proceeded gently. With the reaction carried on, the concentration of free radicals increased gradually, and part of them entered into the micelles. Because the concentration of reaction monomers in the micelles is quite high, auto-acceleration effect of free-radical polymerization happened during this stage, and most of monomers (over 90%) reacted. The residual monomers consumed gradually in the next two or three hours. Due to acrylate emulsion was a metastable system, some of emulsion particles might collide, aggregate and deposit in the last stage.

Fig.2(a) presents the fluorescent acrylate emulsion (AE-TPE-D) and commercial purchased acrylate emulsion under UV light (365nm). Owing to the AIE mechanism as mentioned above, the synthesized AE-TPE-D emitted a strong fluorescence. Fig.2(b) represents the typical morphology of the synthesized fluorescent acrylate emulsion (AE-TPE-D) from TEM measurement. With the packing of micelle formed by emulsifying agent, acrylate monomers and AIE luminogens were dispersed and polymerized in the micelles *via* emulsion polymerization[26]. The fluorescent acrylate emulsion presented typical core-shell structure, in which hydrophobic properties of methylmethacrylate and AIE luminogens were wrapped into the core layer of the fluorescent acrylate emulsion, while the emulsifying agent

with amphipathic property formed the shell layer to make them be dispersed in water. With these characteristics, the composition of the fluorescent acrylate emulsion, the preparation process and the external environment can influence the fluorescence property of the synthesized fluorescent acrylate emulsion. So in the next, we will study the interrelationships between them systematically.

---------- Fig.2 ----------

Fig.2 (a) Fluorescent acrylate emulsion and ordinary acrylate emulsion irradiated under UV light (b) Fluorescent acrylate emulsion observed from TEM measurement

At first, take AE-TPE-D and TPE-containing tetra-acrylate as examples, the interaction between AIE luminogen and polymer chains was studied, and their fluorescence spectra were presented in Fig.3. As we know the result of fluorescence spectroscopy was the relative value, the contents of AIE luminogens of two samples were identical to study their fluorescence properties. Compared to pure TPE-containing tetra-acrylate in THF-water (1:99) mixture, the emission peak of AE-TPE-D is at about 455nm, which blue shifted about 30 nm. Also, it should point out that the fluorescent intensity increases by about 7 times for AE-TPE-D at the content of AIE luminogen. It should partly attribute to the wrapping and coiling of rigid polymer chains[27]. As to small AIE luminogen, it tends to aggregate in its poor solvent and radiate fluorescent light when it is induced by UV light, however, their aggregation is activated just by physical stacking. When it is knitted to rigid polymer chains with chemical bond, its intramolecular rotation may be restricted even harder. So higher absorbed energy can be released by fluorescent light, the emission peak tends to blue shift, and the fluorescent intensity also increases.

---------- Fig.3 ----------

Fig.3 Fluorescence spectra of TPE-containing tetra-acrylate in THF-water (1:99) mixture and Fluorescent Acrylate emulsion (AE-TPE-D)

The fluorescent property of fluorescent acrylate emulsion which is affected by the relative content of AIE luminogen is presented in Fig.4. It is obviously that the peak intensity increased linearly with the content of TPE-containing tetra-acrylate for the sample from AE-TPE-A to AE-TPE-D. This is inaccessible to ACQ probes such as

pyrene, where increasing the concentration of probes leads to the formation of excimers or aggregates and consequent fluorescence quenching[28-30]. For AIE luminogens such as TPE-containing tetra-acrylate, aggregation favors emission, and thus allows the enhancing of fluorescence intensity by increasing AIE luminogen loading[31]. However, for the sample AE-TPE-E, its fluorescence intensity decreases when compared to AE-TPE-D. With four functional groups of AIE luminogen, the stability of the synthesized fluorescent acrylate emulsion may be affected by it due to cross linking polymerization. When the content of AIE luminogen extends to a certain limit, some of the synthesized fluorescent acrylate emulsion tends to gather and precipitate due to excessive cross-linking. So it is understandable that the peak intensity of AE-TPE-E is lower than AE-TPE-D because some of AIE luminogens have been precipitated. To confirm this conclusion, we also measured the fluorescence quantum yield(Φ_F) of fluorescent acrylate emulsions varied with the content of AIE luminogen and the results are summarized in Fig.5 and Table 1, respectively. The trend of Φ_F of different fluorescent acrylate emulsions also indicate that the content of AIE luminogens will determine the luminescence behavior of the fluorescent acrylate emulsions, and it increases with the content of AIE luminogen according to AIE mechanism.

---------- Fig.4 ----------

Fig.4 Fluorescence spectra of fluorescent acrylate emulsion varied with the content of TPE-containing tetra-acrylate

---------- Fig.5 ----------

Fig.5 Fluorescence quantum yield(Φ_F) of fluorescent acrylate emulsions varied with the content of AIE luminogen

---------- Table 1 ----------

Table 1 Optical properties of fluorescent acrylate emulsion varied with the content of TPE-containing tetra-acrylate

Fluorescent acrylate emulsions of different sizes varied with the content of emulsifying agent were prepared and studied. Fig.4S presents their particle size and particle size distribution. From Fig.6, the fluorescent intensities increase with the

decreased size of fluorescent acrylate emulsion particles. As is presented in Fig.2(b), the fluorescent acrylate emulsion particles present a typical core-shell structure and AIE luminogens with hydrophobic property are wrapped in the inner core. With the size of fluorescent acrylate emulsion decreasing, the space for segmental motion of polymer chains in the fluorescent acrylate emulsion particles becomes smaller. The restricted movement of polymer chains will strengthen RIR effect of AIE luminogens because it is knitted to rigid polymer chains with chemical bond.

---------- Fig.6 ----------

Fig.6 Fluorescence spectra of fluorescent acrylate emulsion varied with particle size

Sample AE-TPE-D was selected to study the relationship between fluorescent property and the content of fluorescent acrylate emulsion by the addition of water (Fig.7). From Sample AE-TPE-D to Sample R, the fluorescent intensities of the samples increase with the decreased concentration. For the synthesized fluorescent acrylate emulsion, its component and particle size were fixed. According to AIE mechanism, their fluorescent intensity should decrease with the concentration of AIE luminogens. However, contrary to theoretical analysis, its fluorescent intensity increased in fact. We deem that the changed polarity and the squeezing effect of hydrophilic layer may be the reasons for this phenomenon. As the AIE luminogens are knitted to the polymer chains by chemical bonds, their fluorescence properties will be affected by polymer segmental motion. The polarity of system was increased with the added water, which will block the segment motion of hydrophobic polymer chains[32]. In addition, the increased squeeze force of the hydrophilic layer by the added water may enhance this effect. All of these influences can reinforce the RIR effect of AIE luminogens.

---------- Fig.7 ----------

Fig.7 Fluorescence spectra of fluorescent acrylate emulsion(AE-TPE-D) varied with their concentration

Testing temperature was set to be at 25℃, different acrylate emulsions varied with T_g value were studied by fluorescence spectra. From Fig.8(a), by increasing glass transition temperature, the fluorescence intensity increases. In addition, the peak

positions can be changed also. The peak positions of fluorescent acrylate emulsions were at around 455nm when their T_g values were higher than room temperature, while for those fluorescent acrylate emulsions whose T_g were lower than room temperature, their peak positions were at around 470nm. A possible reason is that in the glassy state, the intramolecular motions of phenyl rings of AIE luminogens are restricted to some extent when they are knitted and embedded in the rigid polymer matrices. The energy of the excited state is annihilated through radiation decay, and thus the fluorescent acrylate emulsiones emits efficiently. When the polymers are in the rubbery state, intramolecular motions of AIE luminogens are activated due to the movement of polymer segments and significantly increased free volume in the polymer matrices. The intramolecular motions consume the energy of the excited state. This leads to the weak and red shift of fluorescence emission in the rubbery state of the polymers[11,33].

---------- Fig.8 ----------

Fig.8(a) Fluorescence spectra of fluorescent acrylate emulsiones varied with their T_g values, (b) Fluorescent wavelength & intensity of fluorescent acrylate emulsion varied with their T_g values

SEM images of the coatings cured at room temperature for different fluorescent acrylate emulsions varied with T_g values are presented in Fig.5S. As we know, the process of film formation for ordinary emulsion is carried on as follows: at first, the emulsion particles are aggregated by the evaporation of water; then they tend to be warped and destroyed due to the capillary forces between the gap of emulsion particles; finally, the damaged emulsion particles tent to intermix with each other and form a flat coating on the substrate surface. T_g value of emulsion can determine the film forming ability of the emulsion particles. For those emulsion particles whose T_g value lower than room temperature, soft polymer chains benefit to the deformation of emulsion particles and form a flat coating. While for those emulsions with high T_g value (beyond room temperature,25℃), the emulsion particles cannot wrap due to stiff polymer chains, and they still present as a nano-sized particles after the evaporation of water. According to AIE mechanism, trace amount of AIE luminogen can be used as the fluorescent probe to study the film forming ability of the emulsion particles.

Glass transition is the intrinsic property of amorphous polymers, and it is the macro-reflection of the transformation for the movement of polymer chains, which will affect the materials' use properties and processability[34,35]. According to Molecular Structural Theory, glass transition is the relaxation phenomenon for the amorphous area of polymer materials from freeze state to unfrozen state. At the room temperature under T_g, only atom or functional groups on the polymer chains can vibrate at the equilibrium position. In addition, according to the mechanical properties of the polymer materials, the whole glass transformation region of polymers materials can be divided into "tough" glass state and "soft" glass state. The temperature to identify these two states was brittle temperature (T_b)[36]. For the temperature is lower than T_b, the polymer materials present brittleness property; however, when the temperature is higher than T_b, the polymer materials present extensibility.

As is presented in Fig.9, AE-TPE-P, whose T_g is set as 40℃, is used as the example to study the interrelation between fluorescent property of fluorescent acrylate emulsions and the test temperature. As the segmental motion ability increases with the increased temperature, according to RIR mechanism, intramolecular motions of TPE are activated due to the movement of polymer segments and significantly increased free volume in the polymer matrices. So the fluorescence intensity decreases with the increased test temperature. It should be pointed out that there are two apparent lowering platforms for the decreased PL intensity in the glass transition region. As is discussed above, there are "tough" glass state and "soft" glass state of the amorphous polymers. Although the subtle changes varied with temperature of the polymer chains cannot be observed from ordinary DSC measurement (Fig.10(a)), however, it might be informed indirectly from fluorescent spectra because the fluorescent probe and polymer chains was knitted together at molecular level with covalent bond, polymer segmental motion can affect the fluorescent luminescence behavior of the fluorescent acrylate emulsions directly. From Fig.10(b), fluorescent intensity of the dried AE-TPE-P varied with test temperature were presented. For polymer matrix, its segmental motion at solid state could not pretty obvious compared to it is dispersed in the emulsion particles due to high packing density of polymer chains at solid state.

From the trend of fluorescence intensity varied with temperature, T_g value of the synthesized emulsion can be obtained, which closes to the theoretical calculation value.

---------- **Fig.9** ----------

Fig.9 (a) Fluorescence spectra of fluorescent acrylate emulsion (AE-TPE-P, T_g=40℃) varied with the testing temperature, (b) fluorescent intensity of AE-TPE-P varied with the testing temperature

---------- **Fig.10** ----------

Fig.10 Study the properties of the dried AE-TPE-P powers by different testing methods (a) DSC thermograms; (b) Fluorescence spectra

Conclusion

Due to AIE luminogen tetraphenylethene-containing tetra-acrylates is knitted with polymer chains by chemical bond, and the synthesized fluorescent emulsion particles are dispersed in water uniformly, the changes of the emulsion system and the segmental motion of polymer matrix will affect the fluorescent properties of AIE luminogen owing to the restriction of intramolecular rotation (RIR) effect. With this characteristic, the process of emulsion polymerization can be monitored on real-time, and the changes with its internal characteristics and external environments can interfere fluorescence spectrometry of the emulsion directly. This study thus opens up a new avenue for the research of the emulsion polymerization process and develops AIE-active emulsion. In addition, the synthesized emulsion with the properties of fluorescence may broaden the application of AIE mechanism.

Materials

THF was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. 4,4'-dihydroxybenzophenone, zinc powder, titanium(IV) chloride(TiCl4), triethylamine, acryloyl chloride, methylmethacrylate (MMA,C.P.), ethylhexyl acrylate(2-EHA,C.P.), dodecyl sulfate(SDS, A.R.), and potassium persulfate(KPS, A.R.) were used as received without further purification.

Instruments

^{1}HNMR spectra were measured on Bruker ARX 400 NMR spectrometers using

$CDCl_3$ as the deuterated solvent and tetramethylsilane (TMS; δ=0ppm) as the internal standard. FTIR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Relative number (M_n) and weight-average (M_w) molecular weights and polydispersity indices (PDI or M_w/M_n) of the fluorescent emulsion particles were estimated by a Waters Associates Gel Permeation Chromatography (GPC) system equipped with RI and UV detectors. THF was used as the eluent at a flow rate of 1.0 mL min^{-1}. A set of monodispersed linear polystyrenes covering the molecular weight range of 10^3~10^7 were used as the standard for the molecular weight calibration. DSC measurements were carried out using DSC Q100 (TA Instruments) (TA Instruments, USA) over the temperature of -50℃ to 150℃ at a scan rate of 10℃ min^{-1} . The thermogram was base line corrected and calibrated using Indium metal. The experimental specimens (8–10 mg) were dried at 60℃ under vacuum for 24h, before being measured. All the samples were firstly annealed at 120℃ for 3 min, and cooled to -50℃ by using liquid nitrogen and then scanned for the measurement. UV-vis absorption and light transmission spectra were measured on a Milton Roy Spectronic 3000 array spectrophotometer. Fluorescence spectra were recorded using a steady state spectrometer (Edinburgh Instrument Ltd, FLSP920) equipped with a temperature control system (Oxford instruments). To eliminate the interference of heating rates on the thermal properties of the fluorescent elastomer, heating rate was fixed at 1 min^{-1} for all specimens. Fluorescence spectra were scanned every 1 min.

The absolute Fluorescence quantum yield(Φ_F) of fluorescent acrylate emulsions was measured using an integrating sphere (FLS 980, Edinburgh). Images of scanning electron microscopy(SEM) was taken on a JSM-6700F electron microscope. Image of and transmission electron microscope(TEM) was taken on JEOL 2010 transmission electron microscope (TEM) at accelerating voltages of 200K /v. Particle sizes of the fluorescent emulsion particles were measured on a Brookhaven Instruments Corporation 90 Plus/B1-MAS Zetaplus Zeta Potential Analyzer.

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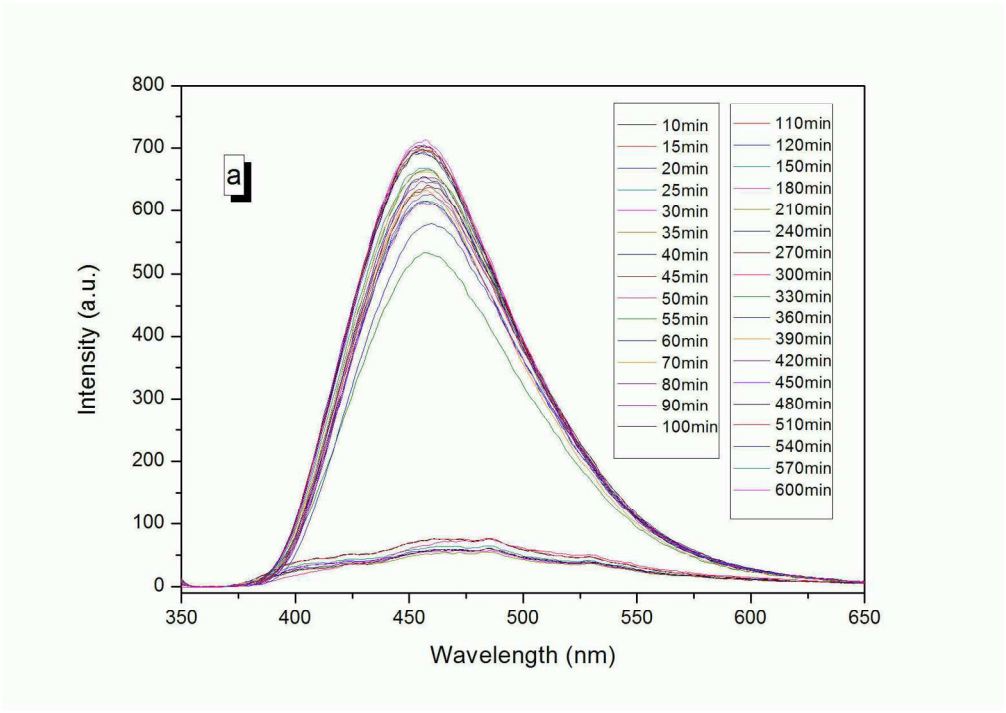


Fig.1(a) Fluorescence spectra of ongoing reacting fluorescent acrylate emulsion

464x328mm (96 x 96 DPI)

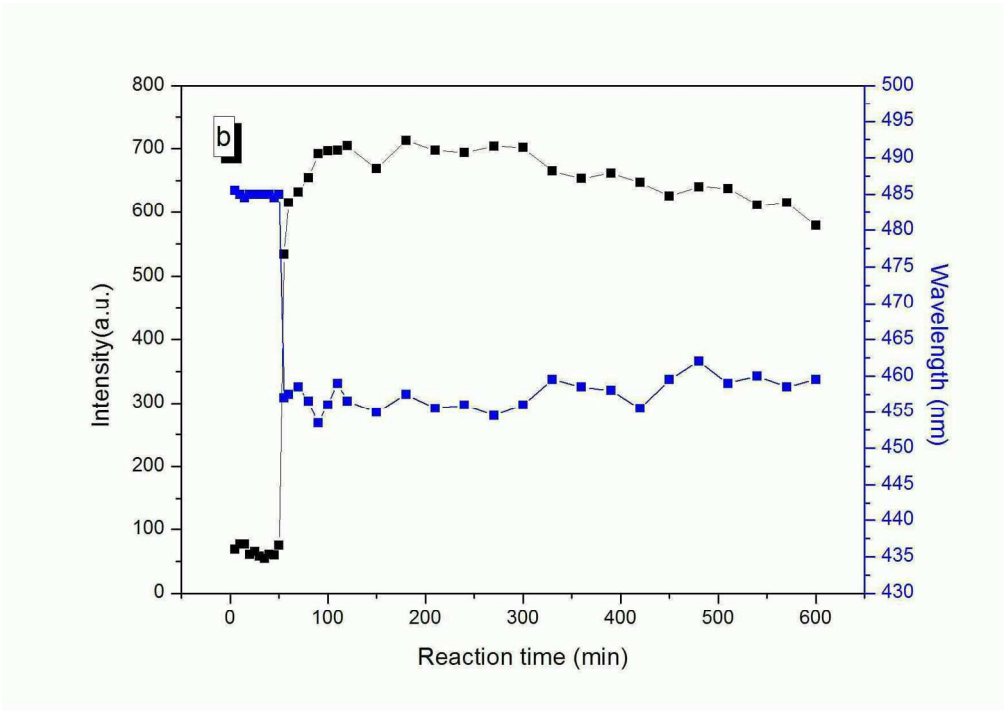


Fig.1(b) Wavelength and intensity of PL spectra of ongoing reacting fluorescent acrylate emulsion

464x328mm (96 x 96 DPI)

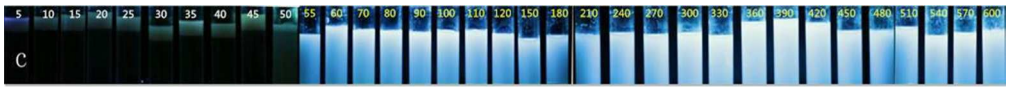


Fig.1 (c) Pictures of ongoing reacting fluorescent acrylate emulsion taken by camera varied with reaction time (From 5 to 600min)

271x21mm (96 x 96 DPI)

Fig.2 (a) Fluorescent acrylate emulsion and ordinary acrylate emulsion irradiated under UV light

163x128mm (96 x 96 DPI)

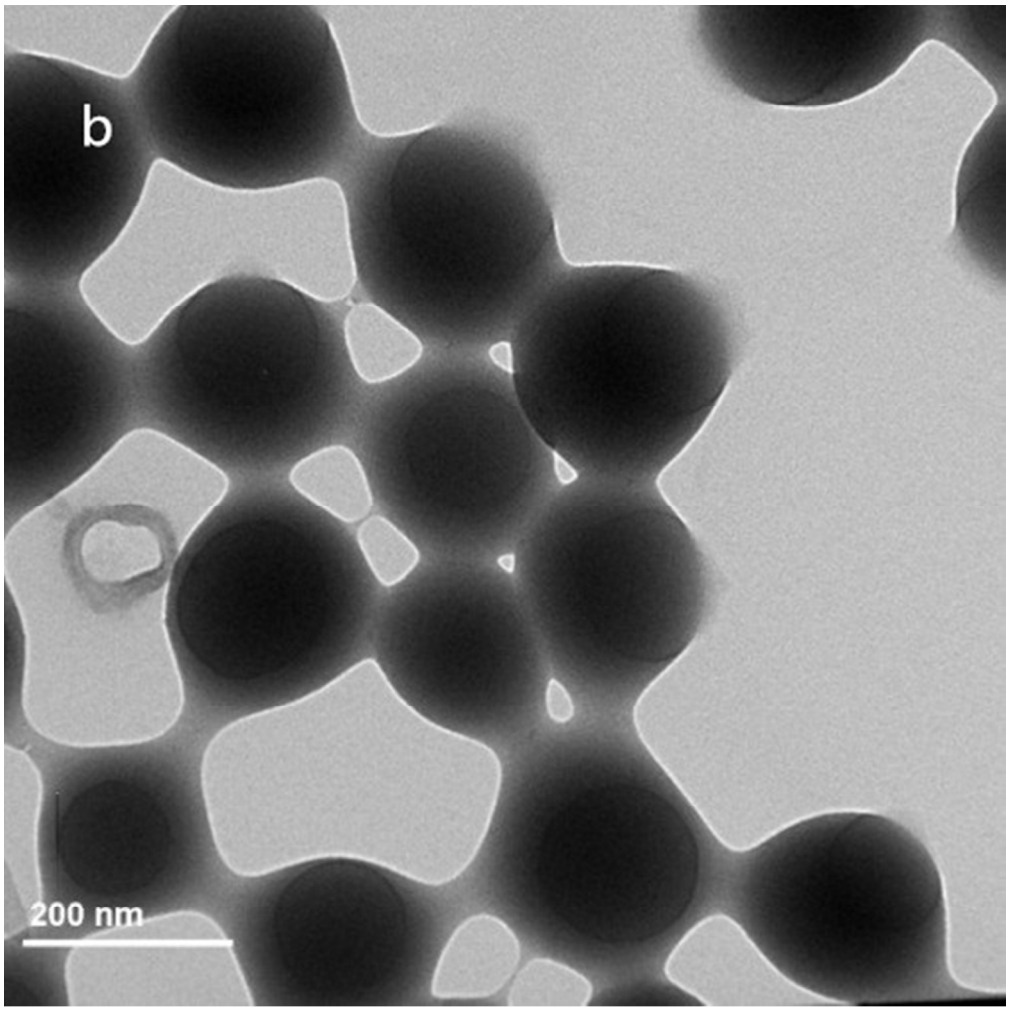


Fig.2 (b) Fluorescent acrylate emulsion observed from TEM measurement

134x134mm (96 x 96 DPI)

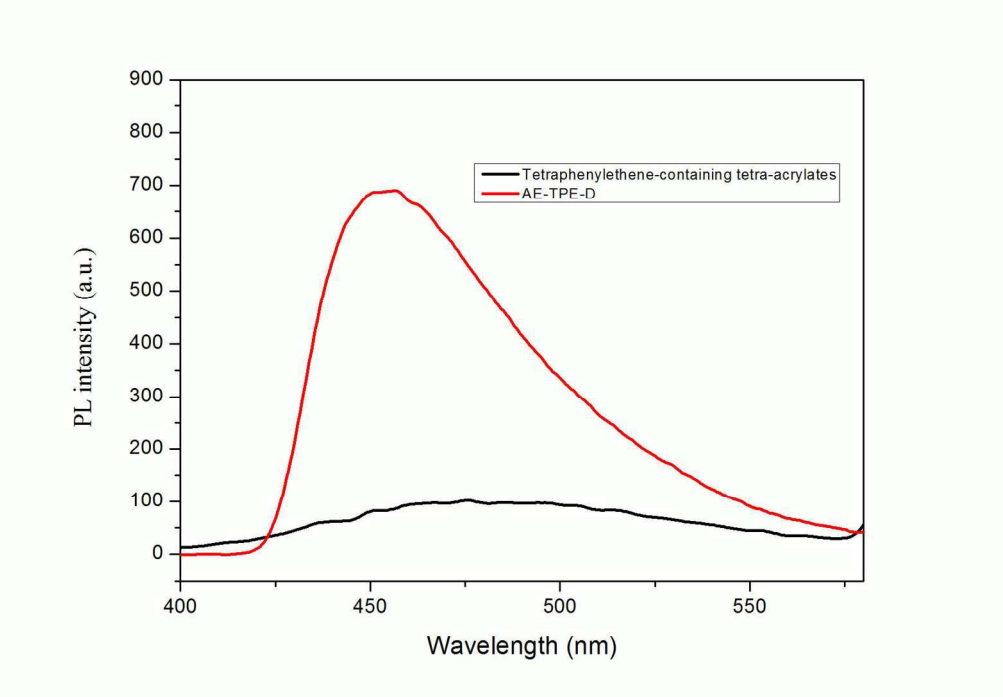


Fig.3 Fluorescence spectra of TPE-containing tetra-acrylate in THF-water (1:99) mixture and Fluorescent Acrylate emulsion (AE-TPE-D)

464x324mm (96 x 96 DPI)

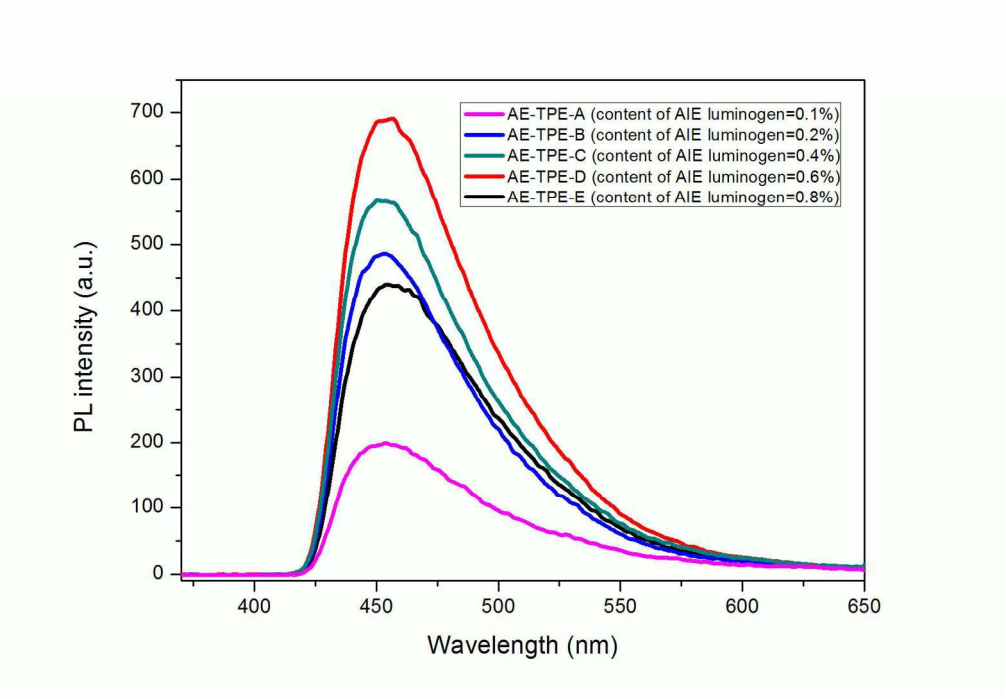


Fig.4 Fluorescence spectra of Fluorescent Acrylate emulsion varied with the content of TPE-containing tetra-acrylate

464x324mm (96 x 96 DPI)

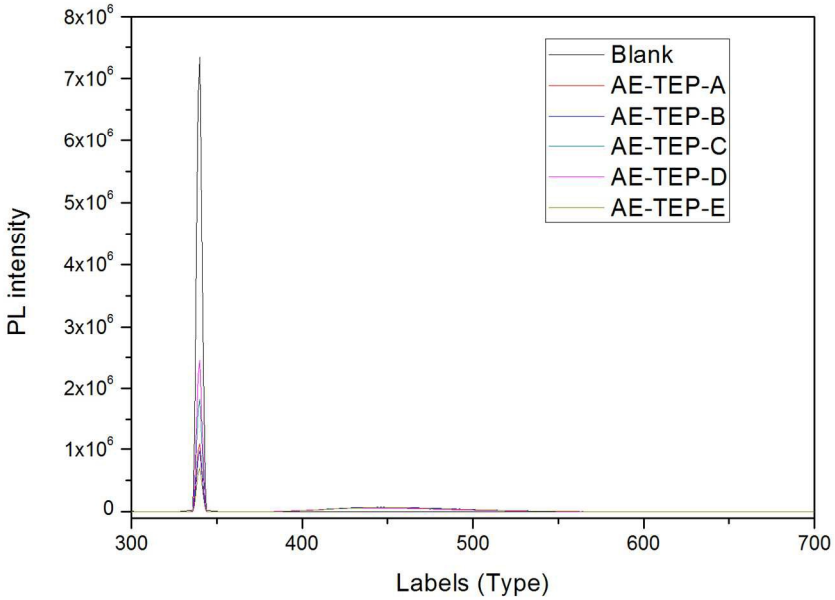


Fig.5 Fluorescence quantum yield(ΦF) of fluorescent acrylate emulsions varied with the content of AIE luminogen

289x202mm (150 x 150 DPI)

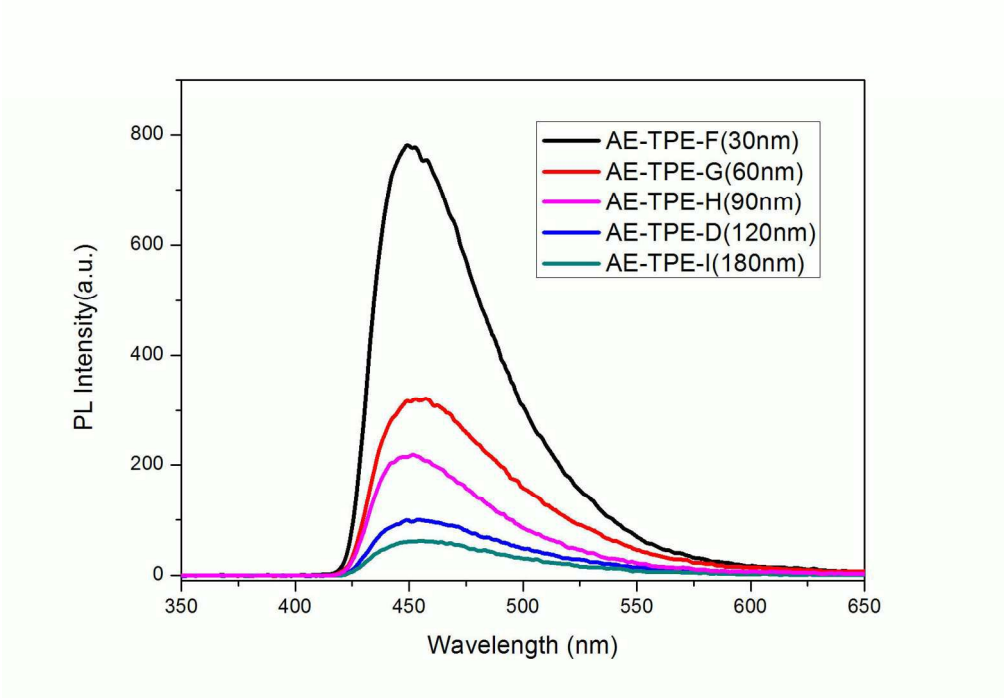


Fig.6 Fluorescence spectra of fluorescent acrylate emulsion varied with particle size

464x324mm (96 x 96 DPI)

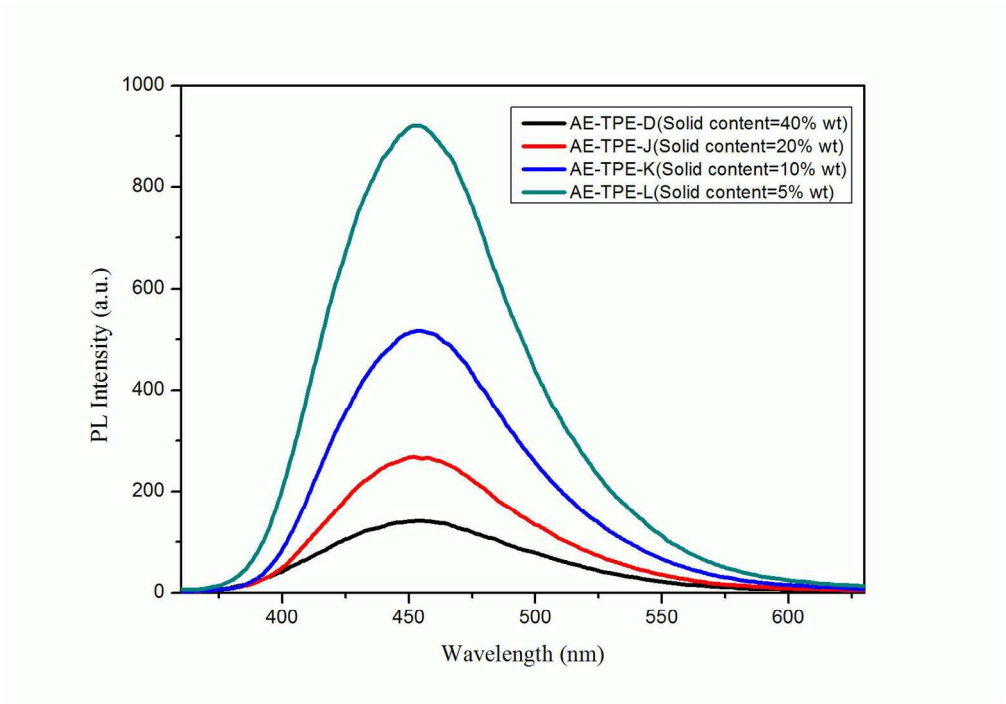


Fig.7 Fluorescence spectra of fluorescent acrylate emulsion(AE-TPE-D) varied with their concentration

464x328mm (96 x 96 DPI)

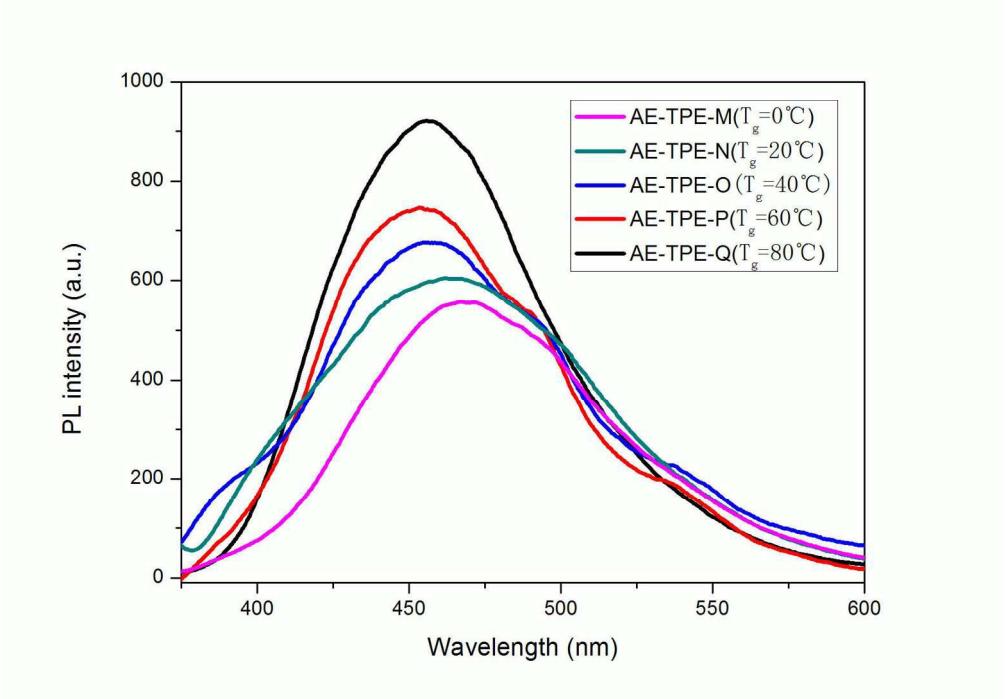


Fig.8(a) Fluorescence spectra of fluorescent acrylate emulsiones varied with their Tg values

464x324mm (96 x 96 DPI)

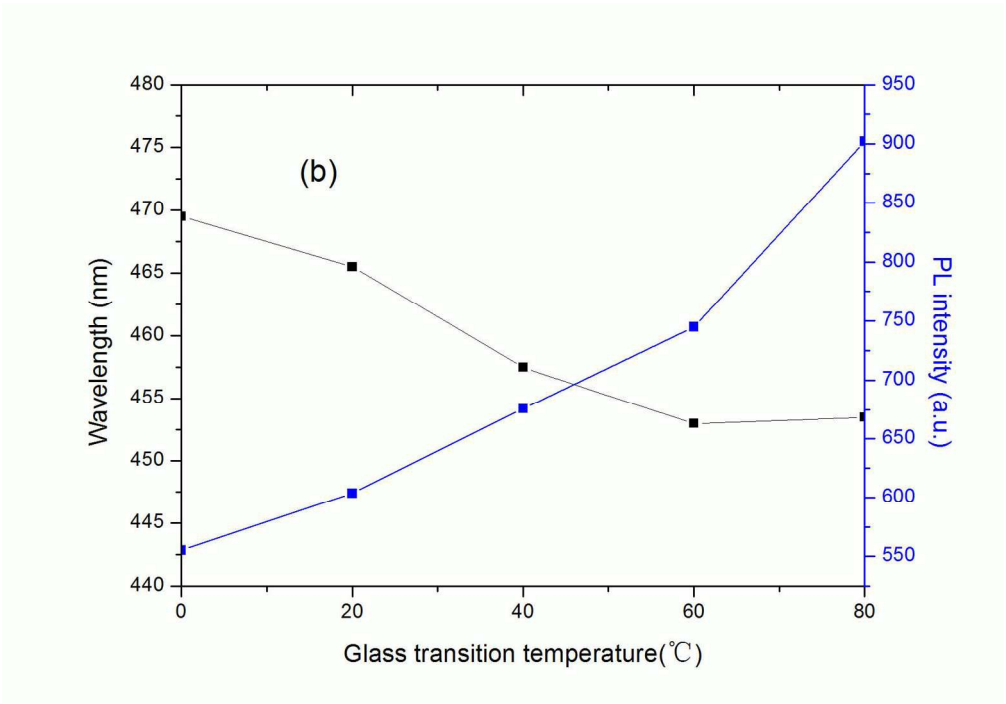


Fig.8 (b) Fluorescent wavelength & intensity of fluorescent acrylate emulsion varied with their Tg values

464x324mm (96 x 96 DPI)

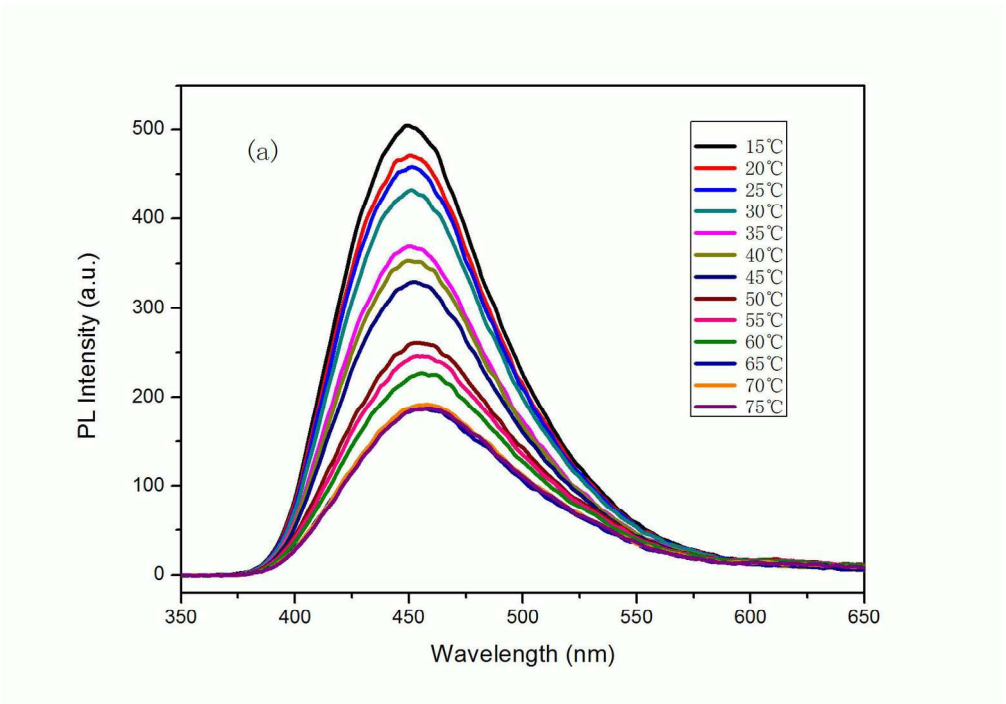


Fig.9(a) Fluorescence spectra of fluorescent acrylate emulsion (AE-TPE-P, Tg=40℃) varied with the testing temperature

464x328mm (96 x 96 DPI)

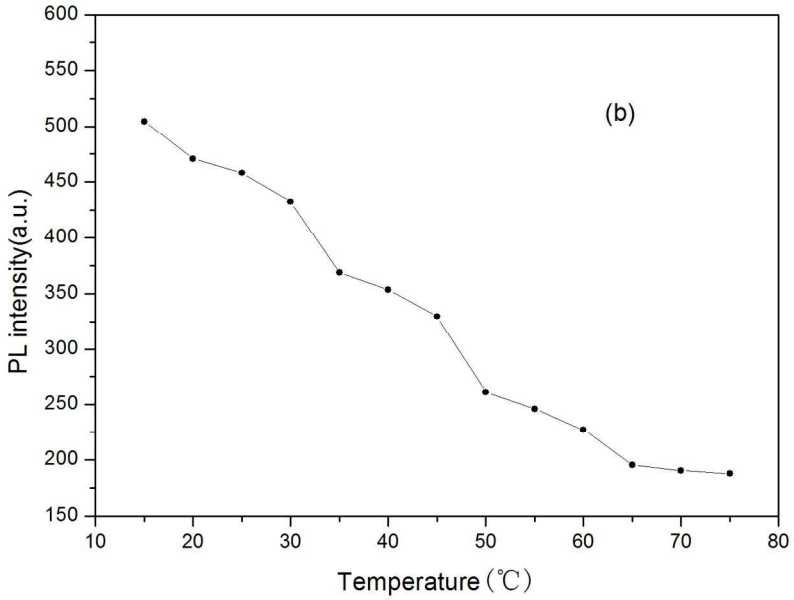


Fig.9 (b) fluorescent intensity of AE-TPE-P varied with the testing temperature

464x324mm (96 x 96 DPI)

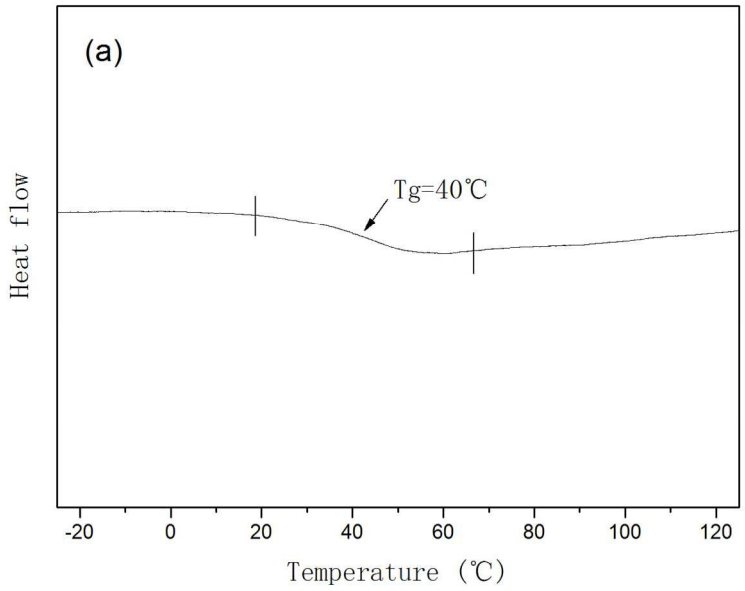


Fig.10 Study the properties of the dried AE-TPE-P powers by different testing methods (a) DSC thermograms

450x314mm (96 x 96 DPI)

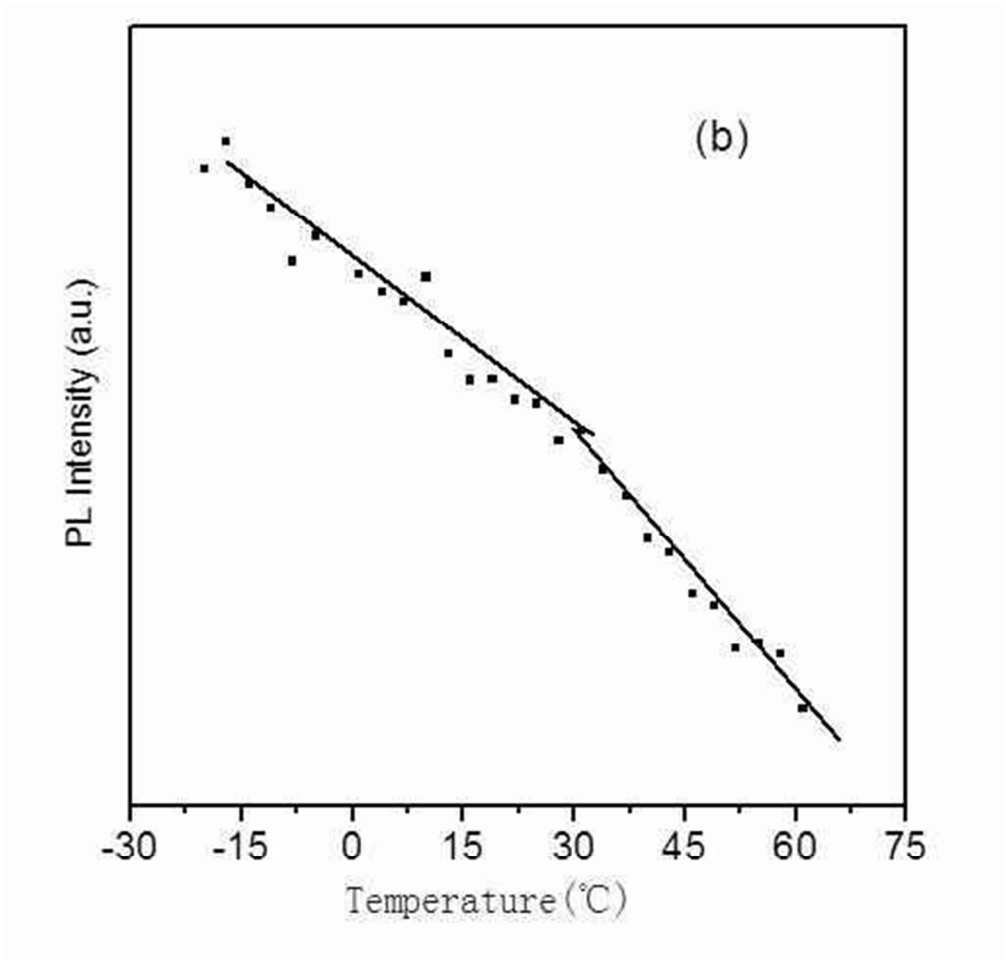
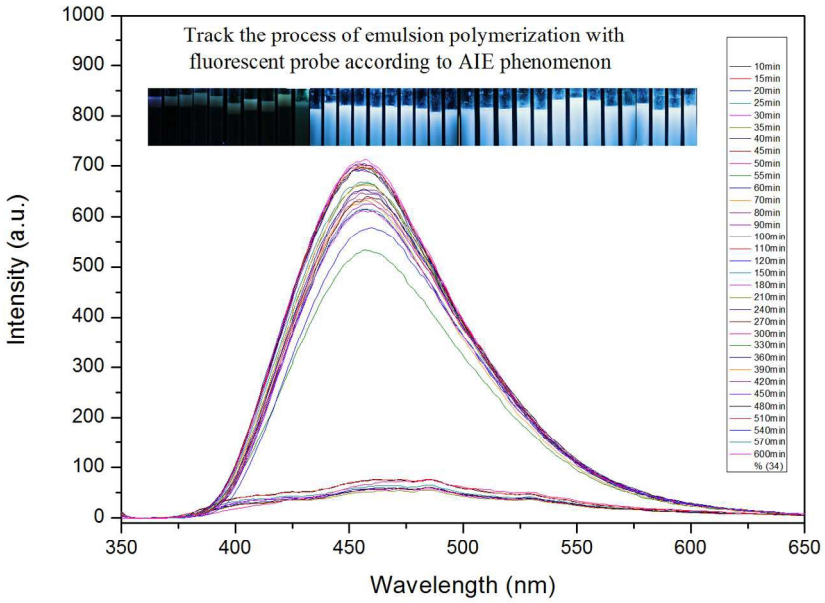


Fig.10 (b) PL intensities of dried AE-TPE-P varied with test temperature

135x129mm (96 x 96 DPI)



464x328mm (96 x 96 DPI)