

## **Grafting Polymerization of Acrylonitrile onto LDPE Film: Study on Grafting Chain Length and Density with UV-vis Spectroscopy**

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### **Summary**

Grafting polymerization of acrylonitrile onto low density polyethylene film was studied further following the earlier work [1]. A novel and effective method was developed to directly determine the number of end-groups, i.e. phenyls at the end of grafted chains with UV-vis spectroscopy; according to the number of phenyl end-groups and the weight of grafted polymers, grafting chain length and density were estimated; investigations indicated both of these two parameters could be practically controlled.

### **Introduction**

Polymer surface modification is of prime importance in polymer applications from the viewpoint of both academics and industries [2]. Chemical and physical surface structures may be altered and controlled by different methods. From these, surface grafting polymerization has attracted much attention of scientists due to its distinct advantages, e.g. forming fast covalent bonds between the new grafting layer and the substrate surface with little damage to the material's bulk properties [3-7]. Surface grafting polymerization can be initiated either by free radical or ionic reactions. Free radical graft polymerization is a versatile method due to its significant advantages: low cost operation, mild reactions, and wide selection of different monomers. It is important to control the grafting chain length and density in many areas of applications, e.g. colloid stabilization, adhesion, lubrication, and tribology [2]. However, it is difficult to control the grafting chain length and density with conventional free radical polymerization, but A. Ramakrishnan et al. successfully prepared surface with controlled graft chain length and density through living radical polymerization [8-12]. Nevertheless, there is still a great problem: the grafting chain length cannot be directly determined at present and it can be only estimated by measuring the molecular weight of the corresponding homopolymer.

In our previous work [1], we designed and investigated a facile sequential grafting polymerization of acrylonitrile (AN) onto low density polyethylene (LDPE) film. In the first step, benzoyl peroxide (BPO) was adsorbed onto the substrate. In the subsequent step, monomer AN and the substrate containing BPO were put into the grafting copolymerization vessel, which was designed by our laboratory, and then BPO initiated the grafting polymerization under heat. Moreover, we proposed that the mode of termination of the grafting polymerization should be by the combination of a growing polymeric radical and a phenyl radical, and we further demonstrated it by UV-vis spectroscopy. In other words, we obtained a layer of grafting chains with phenyls as their end groups. In the present work, we attempted to quantitatively determine the number of phenyls in the grafted chains with UV-vis spectroscopy according to the famous Lambert-Beer Law and estimated the grafting chain length and density. Moreover, we investigated the effects of reaction time, concentration of BPO, and temperature on the grafting chain length and density.

## Experimental Part

### *Materials*

BPO was obtained from Beijing Chemical Reagents Company and recrystallized twice from the methanol-chloroform mixture and dried in vacuum at room temperature. AN was purchased from Beijing Chemical Reagents Company and purified by distillation under reduced pressure to remove inhibitors. Acetone, *N,N*-dimethylformamide, ethanol, benzene, and toluene were from Beijing Chemical Reagents Company and used as received. BPO was chemical pure grade and other chemicals were all analytical pure grade. LDPE films (90  $\mu\text{m}$  in thickness) were purchased from Beijing Plastic Company. The films were first cut into circular shape about 35 mm in diameter, and then subjected to Soxhlet extraction with acetone for 24h to remove impurities and additives.

### *Grafting Polymerization Procedure*

Grafting polymerization was carried out in a polymerization vessel designed by our laboratory, and the main procedure was as follows: In the first step, LDPE film was immersed in toluene solution containing BPO (0.25-1.00%) for 30 s and dried in vacuum at room temperature to constant mass. In the second step, monomer AN and LDPE film containing BPO were placed in the grafting polymerization vessel; the grafting polymerization vessel was subsequently purged with nitrogen for 5 min, and sealed. Afterwards, the vessel was placed into a water bath at a certain temperature (85-95°C). After a predefined polymerization period, the film was taken out from the grafting polymerization vessel and the residual BPO and AN on the film were extracted by soaking and washing the film in acetone and drying the film at room temperature in air. The more detailed procedure was reported in the preceding article [1].

Two parameters, grafting degree (*Gd*) and grafting efficiency (*Ge*) were determined according to the following equations:

$$Gd = (M_1 - M_0) / M_0 \times 100\% \quad (1)$$

$$Ge = (M_1 - M_0) / [(M_1 - M_0) + M_h] \times 100\% \quad (2)$$

where  $M_0$ ,  $M_1$ , and  $M_h$  are the mass of the blank film, the grafted film, and the AN homopolymer, respectively.

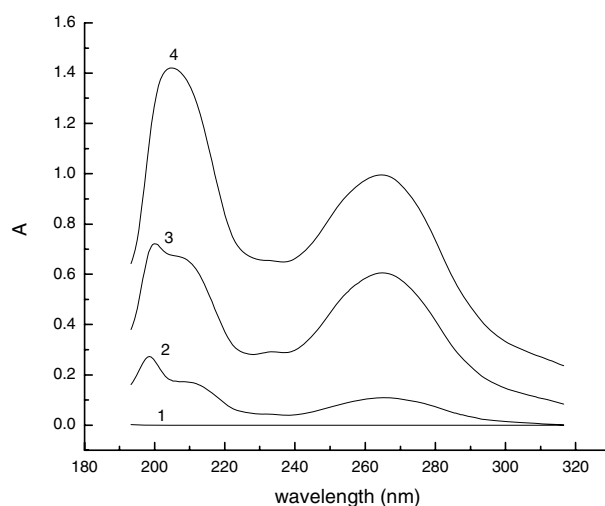
### UV-vis Spectroscopy

The LDPE films bearing BPO and the grafted films were characterized by a UV-vis Spectrometer (GBC CINTRA 20 Australia) with a blank LDPE film as reference sample. The test was repeated twelve times for each film on different locations. Then, the average value ( $\bar{A}$ ) of absorption maximum at 206 nm (assigned to phenyls [1]) for each test was calculated.

UV-vis spectra of ethanol solutions containing benzene, toluene and BPO, respectively, with a series of concentration (25, 50, 75, 100, and 125  $\mu\text{mol/l}$ ) were recorded by the UV-vis Spectrometer with ethanol as reference sample.

### Results and Discussion

Heterogeneous radical polymerization exhibits a unique polymerization behavior different from conventional radical polymerization. In literature [13-16], it is reported that macroradicals in heterogeneous system were entrapped and their lifetime was thus extended. Yasutake et al. [17-19] investigated some gas/vapour-deposition polymerizations, which were carried out with monomers in vapour phase and initiators adsorbed on some substrate surfaces. They reported that active species at growing chain ends may be immobilized on the deposit surface and restricted from chain transfer and terminate reactions. In our system, the grafting polymerization was also a gas/vapour-deposition polymerization. The growing chain radicals are rooted mainly on the film surface and the grafting chains may exist mostly in the form of random coil. Because the AN vapour may be the poorest "solvent" to the grafted chains, the grafting chain radicals are very compact and may adopt a globule. Therefore, the growing chain radicals are not easily terminated by bimolecular reactions. On the other hand, the mobility of phenyl radicals is far higher than that of growing chain radicals and benzoyloxy radicals, so a phenyl radical may move to the vicinity of a growing chain radical, and terminate it [1]. Further more, in the spectra of grafted films shown in Figure 1, there are obvious



**Figure 1** UV-vis absorption spectra of blank film (1) and grafted LDPE films: (2)  $Gd=8.2\%$ ; (3)  $Gd=23.4\%$ ; (4)  $Gd=38.1\%$ .

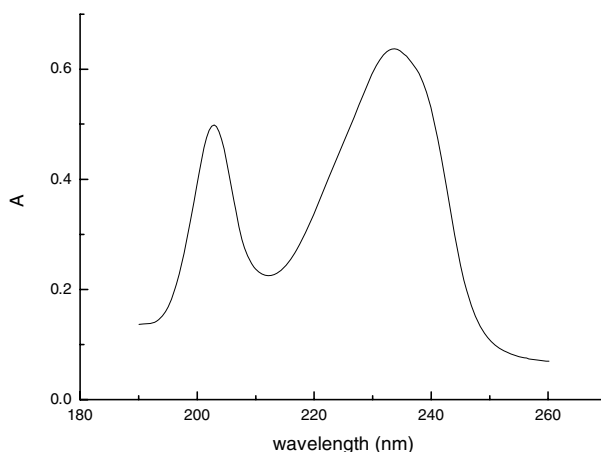
absorption bands at 206 nm, which are ascribed to phenyl groups, and the absorption bands become stronger with the increase of grafting degree. This proves that the end-groups of grafted chains are mainly phenyl groups. According to the analysis above, if we determine the molar number of phenyls on the grafted film and the weight of the grafted polymer, we can estimate the number-average molecular weight of the grafting chains, i.e., the length of the grafting chains. UV-vis spectroscopy is one of the widely used methods in molecular spectroscopy, and Lambert-Beer Law (3) is the basis for the quantitative analysis of it.

$$A = \varepsilon \times c \times b \quad (3)$$

where  $A$ ,  $\varepsilon$ ,  $c$ , and  $b$  are absorbance, molar absorption coefficient, molar concentration and the cell path length, respectively. Based on this law, we designed a set of experiments to determine the molar number of phenyls on the grafted film with UV-vis spectrometer, and the main procedure was as follows: first, the grafted film was characterized by a UV-vis Spectrometer and the average value ( $\bar{A}$ ) of absorption maximum at 206 nm was calculated. Because the size of every film was equal,  $\bar{A}$  was in proportion to the molar number of phenyls on the grafted film. Further more, we obtained an equation (4) according to Lambert-Beer Law (3).

$$\bar{A} = k \times n \quad (4)$$

where  $\bar{A}$  is the average value of absorption maximum at 206 nm for each test,  $k$  is a constant, which is proportional to  $\varepsilon$  for a specific substance, and  $n$  is the total molar number of phenyls on the grafted film. Second, to obtain  $k$  of the grafted film, denoted as  $k_g$ , we took a film bearing adsorbed BPO with the same size and thickness as the control sample for grafted film. We characterized the film containing BPO with the UV-vis Spectrometer under the same conditions for the grafted films (see Figure 2).

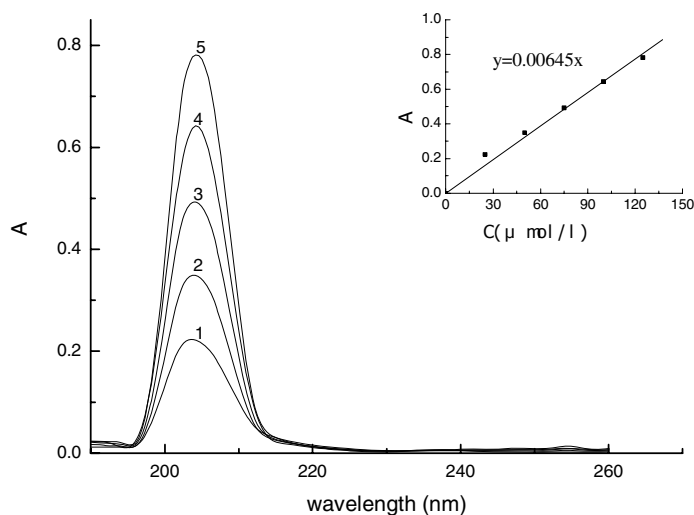


**Figure 2** UV-vis absorption spectrum of LDPE film with BPO.

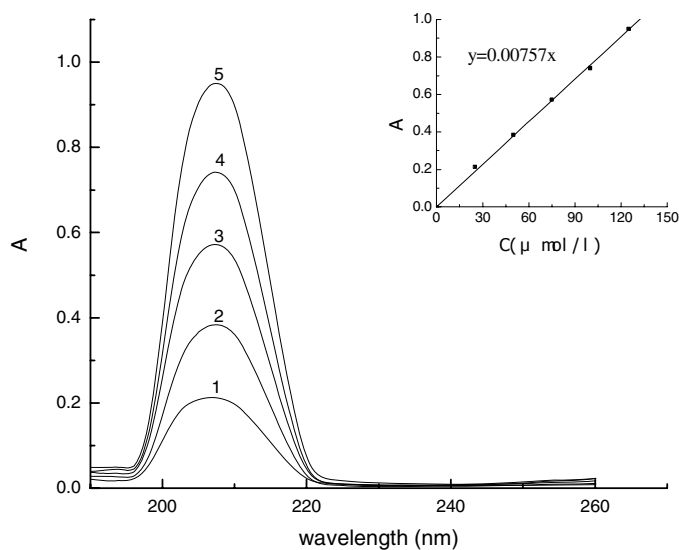
The  $\bar{A}$  of the BPO adsorbing film is also applicable to Equation (4), and the  $n$  of it could be obtained by gravimetric analysis, shown in (Equation (5)).

$$n = \frac{M_2 - M_0}{M} \times 2 \quad (5)$$

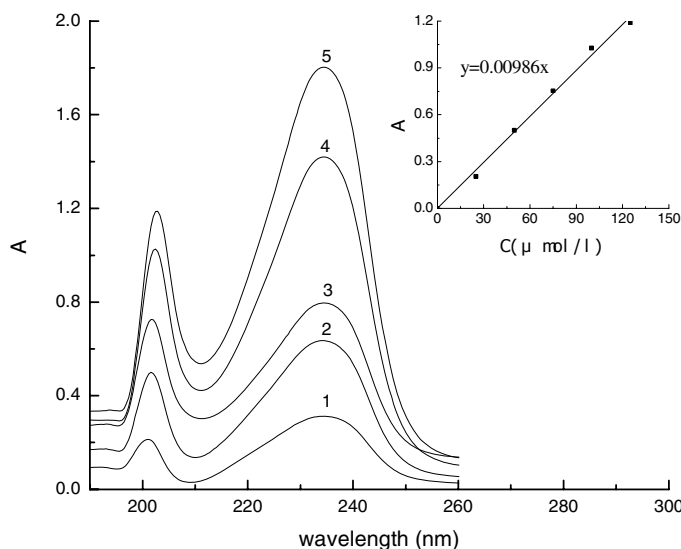
where  $M_0$  and  $M_2$  are the mass of the blank film and the BPO adsorbing film, respectively;  $M$  is molar mass of BPO. From UV-vis spectra of the benzene, toluene and BPO ethanol solution, shown in Figure 3, Figure 4, and Figure 5, benzene has an obvious absorption band at 203 nm, and toluene and BPO also have absorption band at about 203 nm but with a little shift. Therefore, all the absorptions at around 203 nm can be ascribed to the phenyl groups.



**Figure 3** UV-vis absorption spectra of benzene in ethanol solution: (1)  $C = 25 \mu\text{mol/l}$ ; (2)  $C = 50 \mu\text{mol/l}$ ; (3)  $C = 75 \mu\text{mol/l}$ ; (4)  $C = 100 \mu\text{mol/l}$ ; (5)  $C = 125 \mu\text{mol/l}$ . The inset represents the increase in absorbance at about 203 nm as a function of the concentration of ethanol solution.

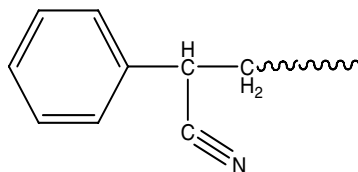


**Figure 4** UV-vis absorption spectra of toluene in ethanol solution: (1)  $C = 25 \mu\text{mol/l}$ ; (2)  $C = 50 \mu\text{mol/l}$ ; (3)  $C = 75 \mu\text{mol/l}$ ; (4)  $C = 100 \mu\text{mol/l}$ ; (5)  $C = 125 \mu\text{mol/l}$ . The inset represents the increase in absorbance at about 203 nm as a function of the concentration of ethanol solution.



**Figure 5** UV-vis absorption spectra of BPO in ethanol solution: (1)  $C = 25 \mu\text{mol/l}$ ; (2)  $C = 50 \mu\text{mol/l}$ ; (3)  $C = 75 \mu\text{mol/l}$ ; (4)  $C = 100 \mu\text{mol/l}$ ; (5)  $C = 125 \mu\text{mol/l}$ . The inset represents the increase in absorbance at about 203 nm as a function of the concentration of ethanol solution.

The assumed end-group structure of the grafted chains in our system is presented in Figure 6, according to resonance stabilization of the growing chain radical.



**Figure 6** Structure of the grafted chain.

Because the phenyl and cyano in the end-groups are not linked directly to each other and there is not appreciable interaction between them, the absorption band of the phenyl in the grafted chain should be equal to that of toluene [20]. According to the reasoning above, we can draw a conclusion that the ratio of  $k_g$  to  $k_b$  ( $k$  of the BPO adsorbing film) could be equal to that of  $\varepsilon$  (toluene) to  $\varepsilon$  (BPO) shown in (Equation (6)).

$$k_g / k_b = \varepsilon (\text{toluene}) / \varepsilon (\text{BPO}) \quad (6)$$

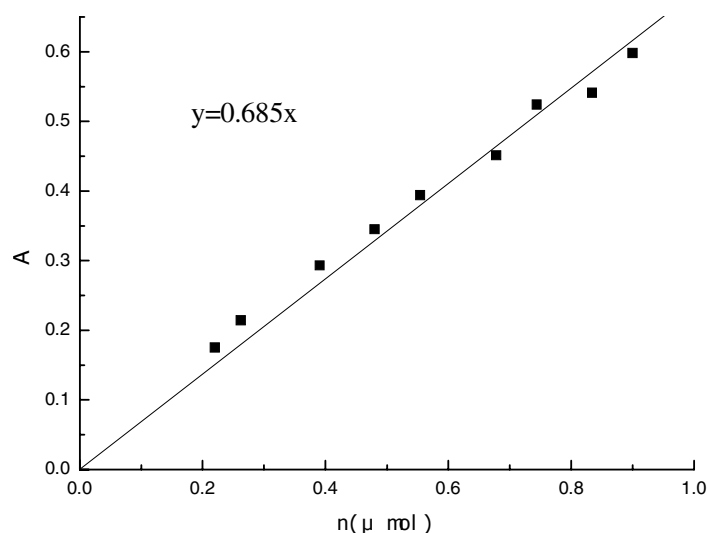
Figure 7 shows a plot of  $\bar{A}$  versus  $n$  for BPO adsorbing films. According to Equation (4), the slope of the plot is  $k_b$  and its value is 0.685. Also, the insets of Figure 4 and Figure 5 show a plot of  $A$  versus  $c$  for toluene solution and BPO solution, respectively. According to Equation (3),  $\varepsilon$  (toluene)/  $\varepsilon$  (BPO) is equal to the ratio of the slopes and the value is 0.768. Therefore, we can calculate  $k_g$  and its value is 0.526 and, according to Equation (4), it is possible to obtain the  $n$  value of grafted films with different  $\bar{A}$ 's. Moreover, we can obtain grafting chain lengths, i.e., the number-average molecular weights ( $\bar{M}_n$ ) and grafting chain density (D), according to Equation (7) and (8):

$$\bar{M}_n = \frac{M_1 - M_0}{n} \quad (7)$$

$$D = \frac{n}{s} \quad (8)$$

where  $M_0$  and  $M_1$  are the mass of the blank film and the grafted film, respectively, and  $s$  is the area of the grafted film.

In our system, the concentration of AN monomer was very low (about 53-68 mmol/l at a temperature between 85-95°C) and the growing chain radicals were highly buried. Therefore, the reactions were less acute and the grafting chain length and density were more controllable. Grafting chain length and density for different polymerization conditions are summarized in Table 1, and grafting degree ( $Gd$ ) and grafting efficiency ( $Ge$ ) are also listed in the table as reference. Grafting chain density listed in Table 1 is far larger than that in some reports [9, 11]. The reason is that because of the high affinity of toluene to LDPE film, BPO located not only on the surface of the film, but also in the subsurface of it, which resulted in that the grafted chains located not only on the surface of the film, but also in the subsurface of it. The grafting chain lengths, i.e., the number-average molecular weights ( $\bar{M}_n$ ) listed in Table 1 are far smaller than the molecular weight of polymers synthesized with conventional radical polymerization [21-23]. The reason may be as follows: first, in our system, the AN monomer concentration was far smaller than the monomer concentration in conventional radical polymerization; second, because the reaction took place not only on the surface of LDPE film, but also in the subsurface of the film, it was difficult for AN molecules to diffuse to the vicinity of a growing chain radical, which decreased the rate of propagation.



**Figure 7** The increase in absorbance at about 203 nm as a function of phenyl molar number of BPO adsorbed on LDPE films.

**Table 1** Variation of grafting chain length and density with polymerization condition

BPO		T (°C)	t (min)	Gd (%)	Ge (%)	chain density (chains/nm <sup>2</sup> )	$\bar{M}_n$
C (%)	D (BPO) <sup>1</sup> molecules/nm <sup>2</sup>						
0.5	2000	85	30	4.36	35.1	120	5500
0.5	2000	85	60	11.1	72.5	200	8600
0.5	2000	85	120	24.2	85.6	260	14000
0.5	2000	85	180	24.8	85.4	280	15000
0.5	2000	90	30	9.96	75.2	560	2800
0.5	2000	95	30	14.7	91.4	1500	1600
0.25	1000	90	30	1.08	78.5	68	7000
0.75	3000	90	30	27.6	73.4	1100	3800
1	4000	90	30	48.9	74.1	2200	3500

<sup>1</sup>D (BPO) was the density of BPO adsorbed on the LDPE film

As seen from Table 1, when the concentration of BPO (C) and temperature (T) are constant, both grafting chain density and  $\bar{M}_n$  increase with the prolongation of the reaction time. The active sites on the surface and in the subsurface of the LDPE film increased constantly with reaction time, which led to the increase of the grafting chain density. In our system, the mode of termination was mainly by the combination of a growing polymeric radical and a phenyl radical [1]. Therefore, the rate of termination was mainly dependent on the number of phenyl radicals and the diffusion rate of them. With the prolongation of the reaction time, both of the two factors decreased, which caused the rate of termination to decrease.

It is also seen from Table 1 that grafting chain density increases with the increase of temperature, but  $\bar{M}_n$  decreases with that. With the increase of temperature, the dissociation of BPO was accelerated, the ability of phenyl radicals to abstract hydrogen atoms from the film increased, and thus the active sites on the surface and in the subsurface of LDPE film increased. Therefore, the grafting chain density increased. At the same time, the number of phenyl radicals and the diffusion rate of them all increased, which resulted in the decrease of  $\bar{M}_n$ .

Variation of grafting chain length and density with BPO concentration are also presented in Table 1. When the temperature was constant, the concentration of AN monomer was also constant. The increase of BPO concentration would increase the active sites. Therefore, grafting chain density increased, but  $\bar{M}_n$  decreased. This accorded well with the general rule of conventional radical polymerization.

One important thing must be pointed out is that there may be some systematical errors in our experiment; for example, there was some change in the size of grafted film from blank film; Lambert-Beer Law is a limiting law for dilute solution. Additionally, we found that when we determined  $\bar{A}$  of the LDPE film having BPO, some of the measurement data with high density of BPO deviated from the standard curve, so when we built the standard curve (Figure 7) we used LDPE film adsorbing low amount of BPO.

In summary, by determining the number of phenyls on the grafted film, we obtained much information about the grafting polymerization, such as initiator efficiency, the grafting chain length and density, and the variations of grafting chain length and density with reaction conditions. According to the experimental results, the grafting chain length and density can be effectively controlled.



## Conclusions

With a simple method, the grafting chain length and density were obtained. Based on the measurement, effects of reaction conditions on grafting chain length and density were investigated; according to these investigations, the grafting chain length and density could be effectively controlled by adjusting the reaction conditions. These results reported here are very useful not only for better understanding the mechanism of radical grafting polymerization, but also for practical applications.

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