Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Yinghai Liu[a]; Jianping Zhang[a]; Rongyue Zhang[a]; Weiqi Zhou[a]; Shengxian Li[a]
[a] College of Chemistry and Environmental Science, Hebei University, Baoding, P. R. China

To cite this Article Liu, Yinghai , Zhang, Jianping , Zhang, Rongyue , Zhou, Weiqi and Li, Shengxian(2007) 'Grafting of 4-Vinyl Pyridine onto Nylon-6 Initiated by Cu(III)', Journal of Macromolecular Science, Part A, 44: 10, 1127 — 1132

To link to this Article: DOI: 10.1080/10601320701524377

URL: http://dx.doi.org/10.1080/10601320701524377

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 1127–1132
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ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320701524377

Grafting of 4-Vinyl Pyridine onto Nylon-6 Initiated by Cu(III)

YINGHAI LIU, JIANPING ZHANG, RONGYUE ZHANG, WEIQI ZHOU, and SHENGXIAN LI
College of Chemistry and Environmental Science, Hebei University, Baoding, P. R. China

Received August, 2006, and Accepted May, 2007

In this article, the graft copolymerization of 4-vinyl pyridine (4VP) onto nylon-6 (PA6) using potassium diperiodacuprate (III) (DPC)–PA6 redox system as initiator is investigated in an alkaline medium. The structure and the properties of graft copolymer are confirmed by Fourier transfer infrared spectroscopy (IR), X-ray diffraction and thermogravimetric analysis (TGA). The mechanism is proposed to explain the generation of radicals and the initiation. The effects of reaction variables, such as the initiator concentration, ratio of 4VP to PA6, pH, as well as reaction temperature and time are investigated. Graft copolymers with high grafting efficiency (>95%) were obtained, which indicated that the DPC–PA6 redox system was an efficient initiator for this graft copolymerization. The quaternized PA6-g-P4VP (QPAVP) is proven to be an excellent adsorbent to heavy metal ions.

Keywords: potassium diperiodacuprate (III); nylon-6, 4-vinyl pyridine; graft copolymerization; redox initiation; adsorption

1 Introduction

Poly(vinyl pyridine) (PVP) is an important class of polymer that exhibits interesting properties due to the presence of the nitrogen atom in the pyridine ring. The weak basic nitrogen atom makes a variety of reactions on PVP, e.g. reaction with acids, quaternization and complexation of metals possible. In addition, these polymers are mainly attractive in applications as polyelectrolytes, polymeric reagents, etc. Graft PVP to fibers to broaden their application received a great deal of attention (1, 2).

As a common engineering plastic, nylon is widely used in many fields including electrical, mechanical, and automotive parts due to its high strength, wear, heat resistance, ease of fabrication and processing. With the continuous development of nylon, the graft modification of nylon attracts more interest. There are some reports on graft copolymerization of vinyl monomers onto nylon using Mn (III), Co (III), Fe (III), peroxomonosulfate-thioglycolic acid redox system, and electron-beam pre-irradiation technique. Grafting polymerization have been considered as an effective method of adding certain desirable properties of PVP to nylon without greatly disturbing the strength and other mechanical properties of nylon. But the report about graft 4VP to nylon, as most of them are completed by traditional chain transfer methods, leads to lower grafting efficiency (3–5).

In recent years, we have obtained some achievements on the graft copolymerization of vinyl monomer initiated by supernormal valence transition metals, such as potassium diperiodatocuprate (III), diperiodatoargentate (III) and potassium diperiodatonickelate (IV) (6–8). It has also been demonstrated that DPC was an efficient initiator for grafting methyl acrylate (MA) or methyl methacrylate (MMA) onto nylon. Here, we first report the synthesis of PA6-g-P4VP copolymer indicated by a DPC-PA6 redox system in alkali medium.

In this article, DPC as oxidant and PA6 as reductant make up the redox system to initiate the grafting copolymerization of 4VP onto PA6. Grafting parameters such as conversion of monomers (PC), percentage of grafting (PG) and efficiency of grafting (PE), is studied, which vary with temperature, monomer concentration, and initiator concentration. The structures and properties of the graft copolymer are characterized by IR, X-ray diffraction, and thermo-gravimetric analysis (TGA).

After the grafting step, ionic character is introduced to the grafted chain by quaternization with benzyl chloride. The hexavalent chromium (Cr (VI)) static adsorption saturation capacity of the QPAVP is also tested. A tentative mechanism is proposed to explain the formation of radicals and the initiation.

2 Experimental

2.1 Materials

PA6 (300–400 mesh, Boye Chemical Factory, Boye, China) was washed with acetone to remove any adhering impurity,

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Address correspondence to: Yinghai Liu, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P. R. China. E-mail: yhliu2004@163.com

and then dried under vacuum at 60°C before use. 4VP (analytical reagent, Fuchen Chemical Plant in Tian Jin) was distilled twice over KOH and CaH_2, respectively, under nitrogen atmosphere. The other reagents were all of analytical reagent and used without any further purification.

2.2 *Synthesis and Measurement of DPC*

DPC was synthesized and measured according to the reported procedure (9). $CuSO_4 \cdot 5H_2O$ (5.53 g), KIO_4 (6.80 g), KOH (9.0 g) were added to about 250 ml of water. The mixture was shaken thoroughly and heated on a hot plate. In about 20 min, the boiling mixture turned intensely red and the boiling was continued for another 20 min more for the completion of the reaction. The mixture was then cooled, filtered through sintered glass crucible (G4) and diluted to 250 ml with doubly distilled water. The concentration of DPC was obtained by its absorption at $\lambda = 414$ nm using a Shimadzu UV-265 spectrophotometer (Japan). The concentration of base DPC was calculated as 1.67×10^{-2} mol/L.

2.3 *Graft Copolymerization*

PA6, a required amount of 4VP, and distilled water are taken in a polymer tube and thermostated at 35°C. The solution is deaerated sufficiently by sparging nitrogen and equilibrated at required temperature with constant stirring. The polymerization is initiated by the addition of calculated DPC. After a required reaction time, the reactant is terminated by aqueous acetic acid solution. The product is filtered from the reaction mixture using weighted sintered glass funnel, washed well with distilled water several times and dried to a constant weight under vacuum at 60°C. This gives the total weight of the grafted polymer with the homopolymer. The homo-polymer is removed from the crude graft copolymer by exhaustive Soxhlet extraction with acetone for 48 h. The final graft copolymer is dried at 60°C to a constant weight under vacuum.

The above process is repeated for the different initiator concentration, 4VP-to-PA6 ratio, pH as well as temperature and time. The grafting parameters, such as PC, PG and GE were defined and calculated as follows:

$$PC/\% = [(W_2 - W_1)/W_0] \times 100$$

$$GE/\% = [(W_3 - W_1)/(W_2 - W_1)] \times 100$$

$$PC/\% = [(W_3 - W_1)/W_1] \times 100$$

Where W_0 is the weight of monomer charged, W_1 is the weight of PA6, W_2 is the total weight of the grafted polymer with the homopolymer and W_3 is the weight of the grafted polymer.

2.4 *Measurements*

The FT IR spectra of the pure PA6 and PA6-g-P4VP are recorded on an FTS − 40 spectrometer (BIO RAD Co., USA) using potassium bromide pellets technique. X-Ray diffraction of ungrafted and grafted PA6 is measured using a Y-4Q X-ray diffraction instrument (Dandong Ray Apparatus Corporation, China). The X-ray diagrams are made with Ni-filtered Cu Ka radiation at 30 KV and 20 mA. TGA curves of PA6 and PA6-g-P4VP are carried out on a Perkin-Elmer apparatus (Pyris 6 TGA) at a heating rate of 20°C/min in a nitrogen atmosphere. The concentration of Cr (VI) is determined by Atomic Absorptin Spectrophotometer (YX-402B Yitong Co., Shenyang China).

3 Results and Discussion

3.1 *Effect of Different Factors on Grafting Parameters*

3.1.1 *Effect of 4VP-to-PA6 Ratio*

The effect of 4VP-to- PA6 ratio on graft copolymerization is depicted in Figure 1. It is observed from this figure that PC and PG increase initially with the increasing 4VP-to- PA6 ratio, but beyond 4VP/PA6 = 2.0, PG increases continuously, while PC decreases. At the same time, GE keeps constant. The initial increasing trend of PC and PG may be explained as follows: the increase of 4VP amount assists in the proximity of monomer to the growing chains and active sites on the PA6. With an increase in 4VP-to-PA6 ratio, PC and PG increase. At the same time, the total volume was fixed. The water volume decreases relatively with the increasing amount of 4VP. So, the DPC concentration in aqueous phase increased. DPC not only reacts with reluctant to produce radicals initiating polymerization of vinyl

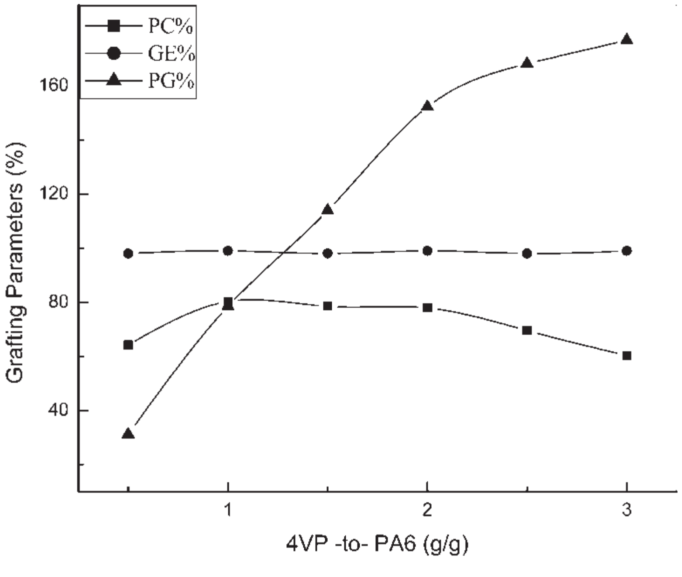


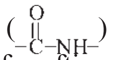
Fig. 1. The effect of the 4VP-to-PA6 ratio. c(DPC) = 6.7×10^{-4} mol/L,T = 180 min, pH = 12.2, Q = 35°C.

monomer, but also reacts with radicals terminating polymerization. When DPC concentration is too large, the result is the reduction of PC. The optimal 4VP-to- PA6 ratio is 2.0.

3.1.2 Effect of Temperature

The grafting reactions were carried out at different temperatures between 25°C and 50°C, keeping the other variables constant. As shown in Figure 2, it is found that GE keeps decreasing slightly. PC increases in the beginning and thereafter increases slightly. PG increases in the beginning up to 35°C and decreases to some extent with further increase in temperature. The improvement in PC and PG may be due to the fact that increasing temperature favors the activation of macroradicals, as well as accelerates the diffusion and mobility of the monomers to the backbone. So PG increases at first. The decline of PG with the increase of temperature can be ascribed both to the acceleration of termination reaction and to increase chance of chain transfer reaction. Accounting for the increasing amount of homopolymer and this is indicated the optimal reaction temperature is 35°C.

3.1.3 Effect of Concentration of DPC

When the other factors are kept invariable, the effect of DPC concentration on graft parameters is shown in Figure 3. With increasing DPC concentration, PC, GE and PG increase. However, beyond the optimum DPC concentration of 6.7×10^{-4} mol/L, they are found to decrease. The initial increasing trend may be due to the fact that in this concentration range, DPC attacks the characteristic group  $\left(\overset{\displaystyle O}{\overset{\|}{-C}}-NH-\right)$ of PA6 backbone directly, and creates a number of grafting sites, which will initiate the grafting in the presence of 4VP. As a result, PC and PG grow sharply. However, an excess of DPC will accelerate the oxidation of radicals by DPC and the propagating chain will be terminated, hence, PC, PG and GE decline.

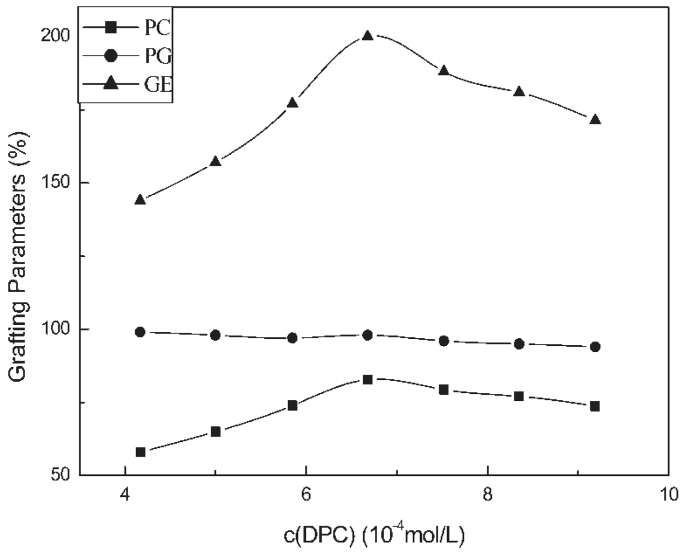


Fig. 3. Effect of concentration of DPC 4VP-to-PA6 = 2.0(g/g), Q = 35°C, T = 180 min, pH = 12.2.

3.1.4 Effect of pH

Potassium hydroxide and hydrogen chloride are employed to maintain required alkalinity in the reaction solution. Figure 4 shows the effect of pH on graft parameters. In the pH range studied, graft parameters changed slightly with pH. They increased slightly at first and then decrease to some extent. These can be explained as follows: DPC exists mainly in the form of c ($H_3IO_6^{2-}$) and c ($H_3IO_6^{3-}$) and the two forms have different activation (10). In the alkali aqueous solution, the ratio of the two forms change with pH, which

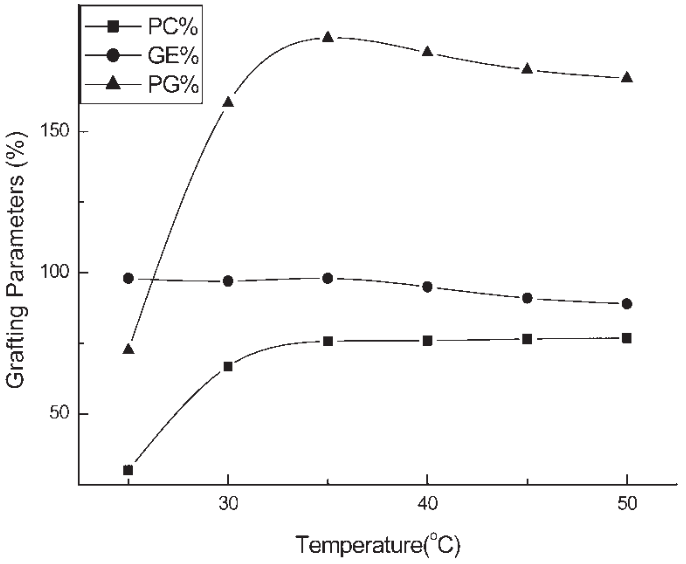


Fig. 2. Effect of temperature. c(DPC) = 6.7×10^{-4}mol/L, 4VP-to-PA6 = 2.0(g/g), T = 180 min, pH = 12.2.

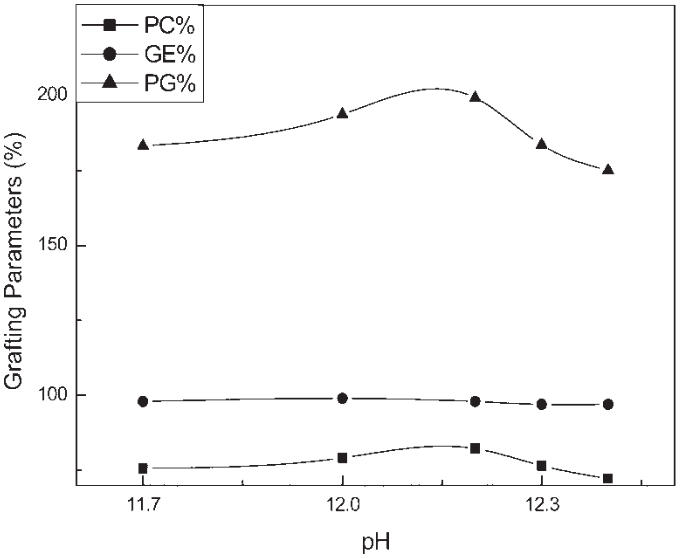


Fig. 4. Effect of pH 4VP-to-PA6 = 2.0(g/g), c (DPC) = 6.7×10^{-4} mol/L, T = 180 min, Q = 35°C.

directly influences the amount of radicals produced in the reaction system. It is found that the optimum pH is 12.2.

3.1.5 *Effect of Reaction Time*

Figure 5 illustrates the influence of reaction time on grafting parameters. It can be seen that GE keeps unchanged during the course of the reaction, whereas PG and PC increase steadily with the reaction time prolonged up to 180 min, and then maintain a plateau, which is consistent with the general rule of conventional radical polymerization. So the optimized reaction time is 180 min.

3.2 Characterization of Graft Copolymer

3.2.1 *IR Spectroscopy*

The IR spectra of the grafted copolymer PA6-g-P4VP, along with pure PA6, is shown in Figure 6. Compared with pure PA6, the final product has characteristic absorption of PA6 at 3300 cm$^{-1}_{(\nu\text{N-H})}$, 1640 cm$^{-1}_{(\nu(\text{C=O})\text{-N})}$, and also has characteristic absorption of P4VP at 1600 cm$^{-1}_{(\nu\text{C=N})}$, 1420 cm^{-1} $_{(\nu\text{C=C})}$ and 823 cm$^{-1}_{(\nu\text{C-N})}$. It is obviously demonstrated that the final product was a graft copolymer of P4VP and PA6.

3.2.2 *X-Ray Diffraction*

The X-ray diffraction spectra of PA6 and PA6-g-P4VP are measured, which are shown in Figure 7. The results of X-ray diffraction illustrate that PA6 has a part of crystal ($X = 0.576$) and PA6-g-P4VP has a part of crystal ($X = 0.235$). These indicate the incorporation of 4VP has changed the crystal structure of PA6, so the crystallizability of the graft copolymer decreased.

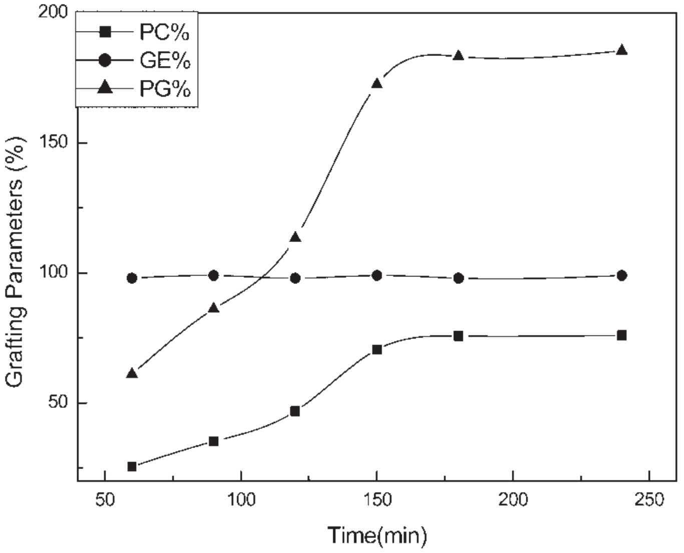


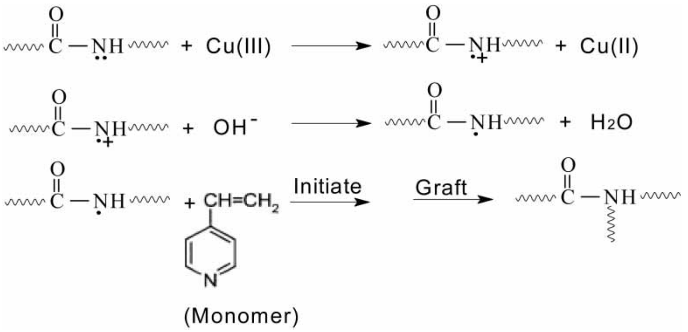
Fig. 5. Effect of reaction time 4VP-to-PA6 = 2.0(g/g), c (DPC) = 6.7×10^{-4}mol/L, pH = 12.2, Q = 35°C.

3.2.3 *Thermal Analysis*

TGA is applied to evaluate the thermal stability of the PA6 (a) and PA6-g-P4VP (b), which was shown in Figure 8. From Figure 8, the TGA of PA6 shows a weight loss in two stages. The first stage, range from 300°C to 500°C shows about 90% loss in weight. This may be attributed to the loss of due to the degradation of the PA6. The second stage is 500°C–650°C with a weight loss of 10% because of carbonization. The TGA of the grafted copolymer, its weight loss shows a complex process. During the first stage from 50°C to 150°C, it is about 3% weight loss, corresponding to the loss of adsorbed and bound water. In the second stages between 300°C and 400°C, there is about 37% weight loss. This may be due to the degradation of P4VP grafted to PA6. In the third stage, weight loss continues up to 480°C with about 47% of the weight random chain PA6. The last stage is from 480°C to 650°C with a weight loss of 10% as a result of carbonization. It illustrated that the grafted copolymer has a distinct different on thermal properties compared to pure PA6, and water retention capacity of PA6 is improved.

3.3 Initiation Mechanism of Grafting Reaction

The FTIR spectrum reveals that 4VP is grafted onto PA6. It may be assumed that DPC react with the characteristic groups ($-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$) on the PA6 backbone to originate macroradicals first and then initiate 4VP grafting polymerization. The initiation mechanism may be shown as follows:



3.4 Quaternization of PA6-g-P4VP and adsorption capacity to Cr (VI)

3.4.1 *Quaternization of PA6-g-P4VP*

A pre-weighed amount PA6-g-P4VP is swelled in a conical flask with ethanol for 24 h. Enough benzyl chloride was added into the under nitrogen atmosphere and kept in a 75°C water bath shaker and the mixtures were agitated for a 6 h interval at a constant speed. Then, the QPAVP is filtered from the reaction mixture using a sintered glass funnel, washed well with ethanol absolute and distilled water several times and dried to a constant weight under vacuum at 60°C (10, 11).

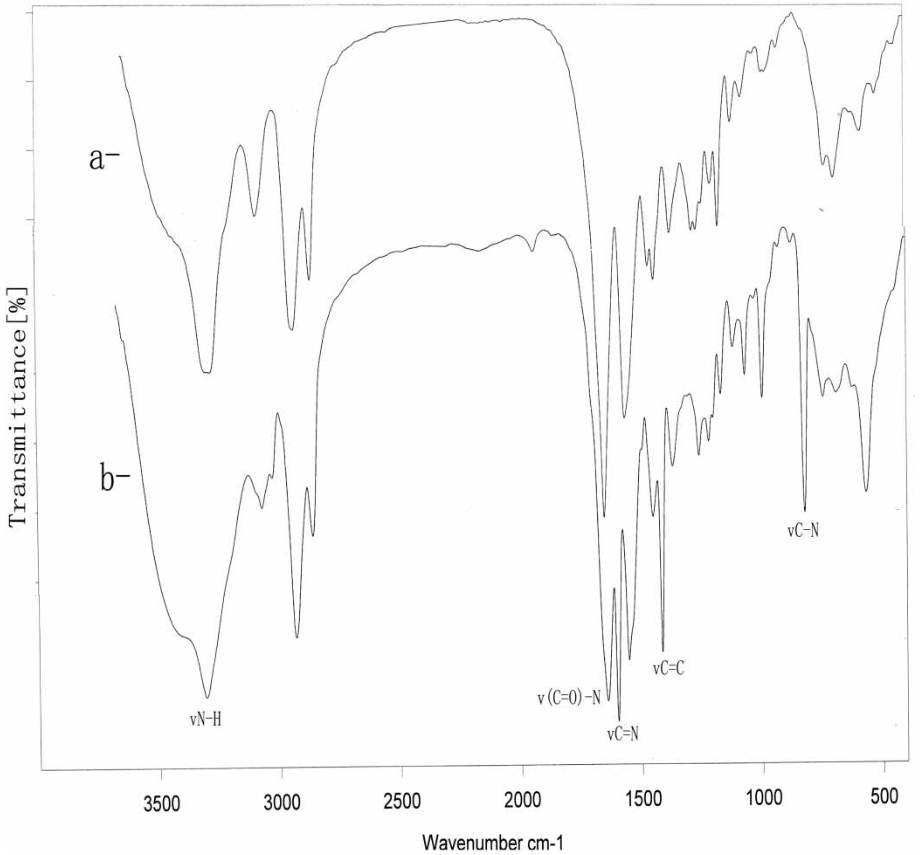


Fig. 6. IR spectra of PA6 (a) and PA6-g-P4VP (b).

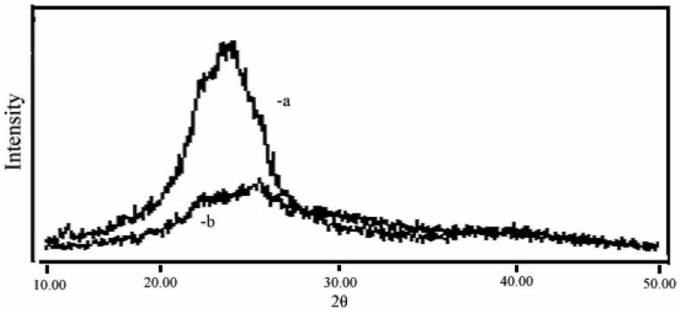


Fig. 7. X-Ray diffraction patterns of PA6 (a) and PA6-g-P4VP (b).

3.4.2 *Cr (VI) Adsorption Capacity*

Adsorption experiments were carried out in conical flasks (100 mL) by agitating a pre-weighed amount of QPAVP with 50 ml of the aqueous Cr (VI) solution of a concentration 4.0×10^{-3}mol/L (1.2 mg/mL). The conical flasks were kept in a 25°C water bath shaker and the mixtures were agitated for 24 h intervals at a constant speed. The solutions were withdrawn at certain time intervals, then the amount adsorbed was calculated based on the analysis of the remaining solutions by atomic spectrophotometer. The adsorption capacity was calculated as follows:

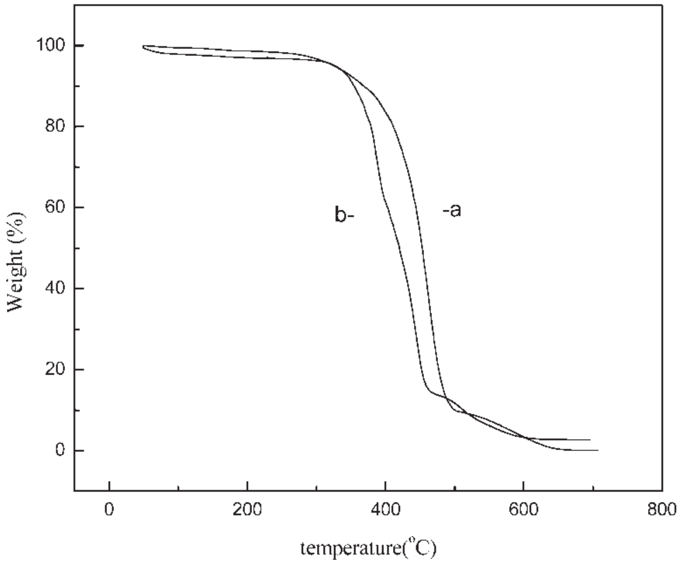


Fig. 8. TGA of grafted and ungrafted polymers a: PA6, b: PA6-g-PVP.

$$Q_e = (C_0 - C_e)V/M$$

Where Q_e is the equilibrium amount adsorbed (mg/g), C_0 the initial concentration of Cr (VI) (mg/mL), C_e the equilibrium concentration of Cr (VI) (mg/mL), M the amount of the QPAVP (mg), and V is the volume of aqueous Cr (VI) solution (12).

The static adsorption saturation capacity $Q_e = 256.7$ mg/g indicates that the QPAVP is an excellent adsorbent for the removal of Cr (VI) from aqueous solution.

4 Conclusions

In this present work, graft copolymers with high graft efficiency were obtained. DPC-PA6 system is found to be an efficient redox initiator for this graft copolymerization. 4VP is successfully grafted onto the PA6 backbone in an aqueous alkaline medium. Compared to the other method, in this method a high grafting effective (>95%) was obtained. The optimal condition is evaluated and listed as follow: 4VP-to-PA6 $= 2.0$ (g/g), c(DPC) $= 6.7 \times 10^{-4}$mol/L, pH $= 12.2$, Q $= 35°$C, time $= 180$ min.

The graft copolymerization can be achieved at a mild temperature and in alkaline aqueous medium. Thus, DPC−PA6 redox system is considered to be a practical initiator, has a good foreground, and the QPAVP is an excellent adsorbent for the removal of Cr (VI) from aqueous solution. Further work is being carried out.

5 Acknowledgements

The authors are indebted to the Natural Science Foundation of Hebei Province for the financial support of this research.

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