

Investigation of Rare Earth Ions Adsorption Properties of PP-*g*-AA

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ABSTRACT: Acrylic acid (AA) was grafted onto the powdered isotactic polypropylene (i-PP) with the electron-beam-induced preirradiation method (Chen, D.-T.; Shi, N.; Xu, D.-F. *J Appl Polym Sci* 1999, 73, 1357–1362). Some rare earth ions, including Sm^{3+} , Nd^{3+} , Eu^{3+} , Gd^{3+} , and Er^{3+} , were adsorbed onto the grafting product PP-*g*-AA. The properties of Sm^{3+} adsorbed were investigated in detail. These properties include the influences of the adsorption time, acidity, ion concentration of the solution, grafting yield of AA onto i-PP, and temperature on the quantity and efficiency of the ion adsorption. Some kinetic and thermodynamic equilibrium constants of the adsorption were obtained in the experiments. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1549–1553, 2000

Key words: polypropylene; electron-beam; preirradiation grafting; rare earth ions; adsorption

INTRODUCTION

Polypropylene (PP) is a kind of widely used polymer material with low density and excellent mechanical property. In recent years, attention was paid to the modification of PP because it greatly broadens the applications of this inexpensive material. When grafted with some functional groups such as acrylic acid (AA), the product PP-*g*-AA exhibits the ability to adsorb rare earth ions in the solution because of the carboxyl groups in the grafted acrylic acid. It can be considered as a polyelectrolyte with weak acidity. The adsorption of rare earth ions onto PP-*g*-AA occurs mainly on the carboxyl groups where H^+ can be displaced by the metal ions in the solution. This property of PP-based material provides the prospect of a new kind of material in which rare earth ions are chemically bonded in the polymer matrix, which

has potential applications such as acting as fluorescent materials. In this article, we investigated the rules of rare earth ion adsorption of PP-*g*-AA. Similar studies on some other polyelectrolytes and metal ions are in progress.

EXPERIMENTAL

Materials

Powdered isotactic PP, with particle size <0.5 mm, was provided by Yanshan Petrochemical Engineering Co., China; acrylic acid, analytical reagent (AR) was provided by Qiuxian Chemical Co., Beijing, China; HAc, HCl, NaOH, chloroethanoic acid, arsenazo III (all AR) were provided by Beijing Chemical Factory, China; NaAc (AR) was provided by Wenzhou Chemical Reagent Factory, China; and Sm_2O_3 was provided by Shanghai Yuelong Organic Metal Co., Ltd., China.

Instruments

The linear electron accelerator Model BF5 (made in Beijing), pH meter Model PHS-3C (Shanghai

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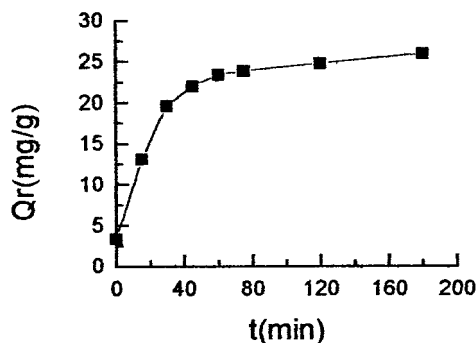


Figure 1 Effect of adsorption time on rare earth ion adsorption quantity.

Second Analytical Instrument Factory), and spectrophotometer Model 721-100 (Shanghai Third Analytical Instrument Factory) were used for measurements.

Synthesis of PP-g-AA

The powdered i-PP was placed in paper bags and irradiated under the electron beam from the linear electron accelerator. The beam energy was 4 MeV; the current was 2×10^{-6} A, and the dose rate was approximately 10^2 Gy/s. The irradiation process was operated at room temperature.¹

A certain amount of preirradiated i-PP, AA, Mohr's salt, and distilled water were introduced into a reaction flask connected with a water-cooling condenser. The flask was immersed in a water bath of 80°C. After 2 h, the sample was filtered and immersed in diluted HCl overnight, and then extracted with distilled water in a Soxhlet extractor for 7 h to remove the homopolymer. The grafted sample was oven dried at 60°C to constant weight. The grafting yield (G) was calculated with

$$G = (W_g - W_0)/W_0 \times 100\%$$

where W_g and W_0 represent the weight of grafted and original i-PP, respectively.

Preparation of Rare Earth Ion Solutions

The solution of desired concentration was prepared by dissolving a certain amount of Sm_2O_3 into HCl, warming, and stirring if needed, then diluting the solutions to required volumes. The accurate concentrations of the solutions were determined by titrating them with EDTA, the concentration of which was determined with the standard solution of Zn^{2+} . Other rare earth ion

solutions containing Nd^{3+} , Eu^{3+} , Gd^{3+} , and Er^{3+} were prepared in a similar way.

Adsorption of the Rare Earth Ions onto PP-g-AA

A solution of 25.00 mL of rare earth ion with a certain concentration, 25.00 mL of HAc–NaAc acid–base buffer, and 2 g PP-g-AA were placed into a beaker. The mixed solution was stirred at a constant temperature for a certain period of time with an electromagnetic stirrer. The grafting yield (G) of PP-g-AA used in the experiments was 65% and the adsorption processes were carried out at room temperature (298 K) unless otherwise specified.

Measurement of Absorbance

Since the concentration (c) of the solution is in direct proportion to its absorbance (A), the concentrations of the solutions could be read on the c – A standard curve.

The absorbance of a series of solutions of definite concentrations was measured with the spectrophotometer by using chloroethanoic acid (0.04 mol/L) as an acid–base buffer and arsenazo III (0.04%) as a dye agent.^{2,3}

Measurement of Acidity

The acidity of the solutions were measured on the pH meter. The required acidity was achieved by adjusting the solution with HCl and NaOH.

RESULTS AND DISCUSSION

Reaction Time

Figure 1 illustrates the effect of reaction time (t) on the adsorption quantity (Q_r). Q_r increases as

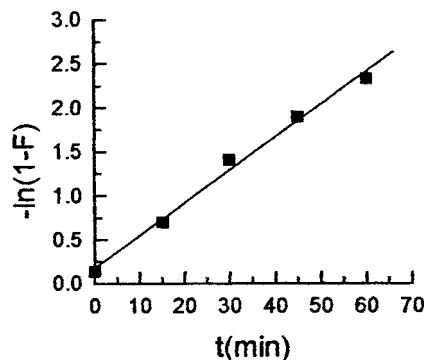


Figure 2 Diagram of $t - [-\ln(1 - F)]$.

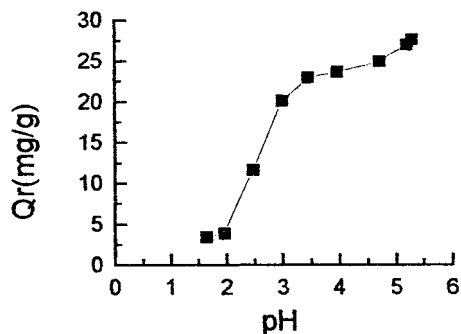


Figure 3 Influence of acidity in the solution on adsorption quantity.

the reaction time extends; however, the curve levels off after the point of 60 min, indicating that in the period as long as about 60 min, the adsorption is already close to saturation. Longer reaction time has no evident effect for PP-g-AA to adsorb more Sm³⁺. Therefore, we chose 60 min as the optimum reaction time in the next experiments.

According to literature,⁴ the rate of adsorption can be calculated by using the equation

$$-\ln(1 - F) = kt$$

where $F = Q_t/Q_\infty$, Q_t and Q_∞ represent the adsorption quantity after time t and in equilibrium, respectively. Since the adsorption was nearly completed after 180 min, we took Q_t where t equals 180 min as Q_∞ .

Figure 2 is the diagram of $t - [-\ln(1 - F)]$. The value of the adsorption rate k is 0.03727 min⁻¹, obtained from the slope of the line.

Acidity

Figure 3 shows the relationship between Q_r and the acidity of the solution.

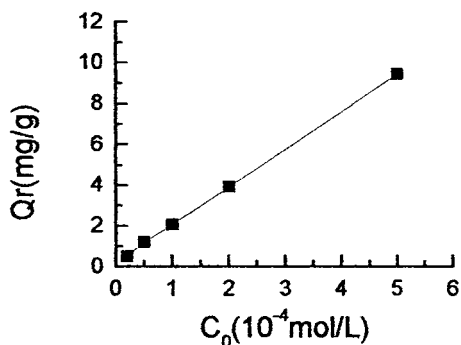


Figure 4 Effect of initial ion concentration on adsorption quantity.

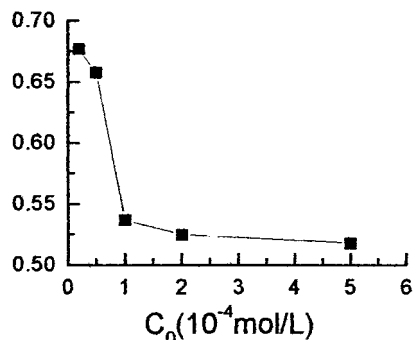


Figure 5 Effect of initial ion concentration on adsorption efficiency.

With the increase in acidity, Sm³⁺ adsorption quantity decreases. The adsorption of rare earth ions onto PP-g-AA can be considered as the competition between the rare earth ions and H⁺ in the carboxyl groups of grafted acrylic acid, which is the actual site of the reaction. When the concentration of H⁺ in the solution increases, the adsorption site is occupied by H⁺ more readily; on the other hand, Sm³⁺ that has already been adsorbed tends to be displaced by H⁺, which is more dominant in the solution. However, for Sm³⁺ and most other rare earth ions, hydrolysis occurs when the pH value of the solution is higher than 5.5. For this reason, we chose HAC-NaAc (pH 5.2) as an acid-base buffer in the experiments.

Concentration of the Solution

The adsorption was conducted in a series of Sm³⁺ solutions with different initial concentrations. Figures 4 and 5 demonstrate the variations of adsorption quantity (Q_r) and adsorption effi-

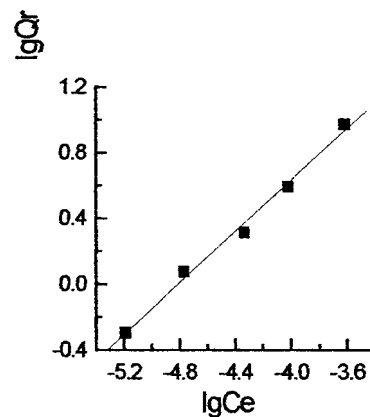


Figure 6 log C_e - log Q_r diagram.

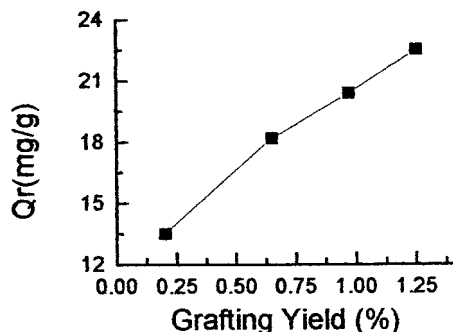


Figure 7 Relationship of grafting yield and adsorption quantity.

ciency (e) with the initial concentration (C_0) of Sm^{3+} .

Within the range of the concentration tested, with the increase in C_0 , Q_r increases linearly, whereas e decreases rapidly in the lower concentration. The cause of this phenomenon might lie in the disproportion of the number of carboxyl groups in the grafted AA to that of Sm^{3+} ions in the solution.

The homothermal curve of the adsorption is shown below; C_e represents the concentration of Sm^{3+} in the solution after adsorption.

According to Freundlich's equation,

$$Q = aC_e^{1/b}$$

or

$$\log Q = (\log C_e)/b + \log a$$

where a and b are both constants. The diagram of $\log C_e - \log Q_r$ is shown in Figure 6.

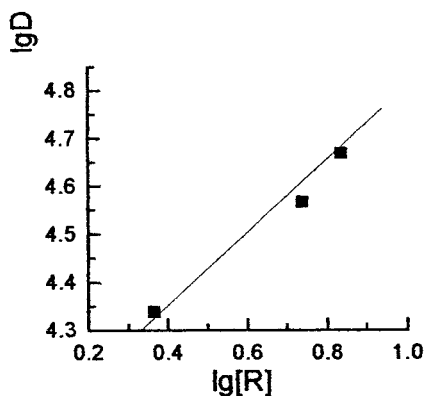


Figure 8 $\log[R] - \log D$ diagram.

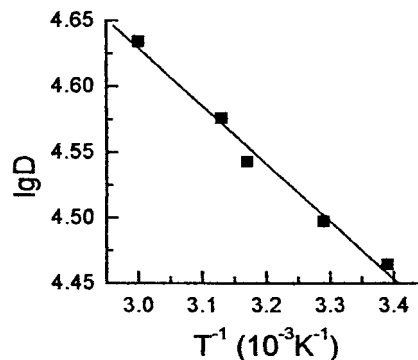


Figure 9 $1/T - \log D$ diagram.

The slope of the line is 0.78, namely $1/b = 0.78$, so $b = 1.28$. When the value for b is between 2 and 10, it is fairly easy for the adsorption to proceed.⁴ Because the value for b here is <2 , we can judge that in our experiment, the adsorption does not take place quite as easily. It probably requires relatively high activating energy.

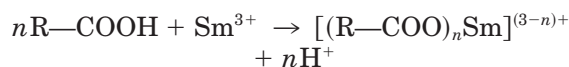
Grafting Yield

The variation of adsorption quantity to the grafting yield is shown in Figure 7.

It can be noted that when the grafting yield equals 0 (i.e., there is no AA grafted onto i-PP), the adsorption quantity equals 3.75 mg/g (this point does not appear on the diagram), indicating that besides chemical adsorption, physical adsorption also exists, although it is only of a small portion.

It is clear that the adsorption quantity increases with the increment of the grafting yield. The higher the grafting yield, which means more carboxyl groups are introduced onto i-PP, the more adsorption sites in PP-g-AA. However, Q_r does not increase linearly; it can be attributed to the steric hindrance. When the number of carboxyl groups in the grafted AA increases, it becomes more difficult for Sm^{3+} in the solution to approach and displace H^+ on the carboxyl groups that are tightly packed. Hence the adsorption efficiency drops.

The adsorption can be expressed as



Since the adsorption was carried out in the acid-base buffer, $[\text{H}^+]$ was constant. On the basis of the equation in literature,⁴

Table I Adsorption Data of Other Ions

Rare Earth Ions	C_0 (10^{-4} mol/L)	Q_r (mg/g)
Nd ³⁺	8.98	0.193
Eu ³⁺	8.60	0.190
Gd ³⁺	8.94	0.221
Er ³⁺	8.61	0.246

$$\log D = \log K + n \log[R]$$

In this equation, D represents the distribution ratio, $D = Q_r/C_e$, where C_e is the metal ion concentration (mg/mL) in adsorption equilibrium; K represents equilibrium constant of the adsorption reaction; n is the average coordination number; $[R]$ is the AA content of PP-g-AA (mmol/g), $[R] = 1000G/[(1 + G) \times M (\text{CH}_2=\text{CHCOOH})] = 13.88G/(1 + G)$.

Figure 8 is the graph of $\log[R] - \log D$, from which we can see the value of $\log K$ is 4.04.

Temperature

In the temperature range of our experiments, a higher temperature favors the adsorption process.

To get thermodynamic equilibrium constants, the $1/T - \log D$ diagram is shown in Figure 9. The slope k of the line is -445 .

As we know,

$$\log D = -\Delta H/(2.303RT) + \text{const.}^4$$

So $\Delta H = -2.303R \times \text{slope} = 8.52$ kJ/mol. The positive value for ΔH indicates that the process is endothermic. $\Delta G = -RT \ln K = -2.303 RT \log K$, and $\Delta S = (\Delta H - \Delta G)/T$. When $T = 298$ K, the values for ΔG and ΔS can be calculated as ΔG

$= -23.1$ kJ/mol, $\Delta S = 106$ J mol⁻¹ K⁻¹. Apparently the reaction occurs spontaneously.

Other Rare Earth Ions

Four kinds of other rare earth ions including Nd³⁺, Eu³⁺, Gd³⁺, and Er³⁺ were adsorbed onto PP-g-AA. The adsorption quantities are listed in Table I.

CONCLUSIONS

PP-g-AA can adsorb many kinds of rare earth ions in the solution. When Sm³⁺ concentration is 10^{-4} mol/L, the adsorption quantity is approximately 20 mg/g and the adsorption efficiency is close to 50%. The adsorption process reaches about 90% completion in 60 min. Low acidity of the solution is a good condition for the adsorption to occur, but rare earth ions will hydrolyze when the pH value is higher than 5.5, so the adsorption should be conducted within the proper acidity range. Initial concentration (C_0) of the rare earth ion solution also affects the adsorption. In the concentration range of our experiments, PP-g-AA tended to adsorb more Sm³⁺ in concentrated solution, whereas the adsorption efficiency dropped when C_0 was high. The higher the grafting yield of AA onto i-PP, the more Sm³⁺ adsorbed onto PP-g-AA. Higher temperature favors the adsorption, indicating that the process is an endothermic one.

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