

# Hg(II) Removal with Polyacrylamide Grafted Crosslinked Poly(vinyl chloride) Beads via Surface-Initiated Controlled/"Living" Radical Polymerization

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**ABSTRACT:** Polyacrylamide grafted crosslinked poly(vinyl chloride) beads (PAM-PVC) were prepared by the surface-initiated controlled/"living" radical polymerization (SI-CLRP) methodology from the crosslinked poly(vinyl chloride) beads with surface modification with diethyldithiocarbamyl groups under UV irradiation. The macroiniferter, diethyldithiocarbamyl crosslinked poly(vinyl chloride) beads (DEDTC-PVC) were prepared by the reaction of the surface C—Cl groups with sodium *N,N*-diethyl dithiocarbamate. The "grafting from" polymerization exhibited some "living" polymerization characteristics and the percentage of grafting

(PG%) increased linearly with polymerizing time and achieved 47.6% after 6 h UV irradiation. The beaded polymer with polyacrylamide surface was also characterized with Fourier transform infrared (FTIR) and scanning electron microscope (SEM). Its adsorption property for Hg(II) ion was also investigated preliminarily. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3385–3390, 2006

**Key words:** polyacrylamide; crosslinked poly(vinyl chloride) beads; surface-initiated controlled/"living" radical polymerization; macroiniferters; adsorption properties

## INTRODUCTION

The modification of surfaces is an important means of tailoring the physical and chemical properties of materials. A widely used method for modifying the surface of microspheres is depositing or spraying a polymeric coating from a solution, which normally can provide only comparatively crude control of the structural and surface properties of materials. Other frequently used methods such as polyelectrolyte deposition, plasma deposition, and polymerization within a Langmuir-Blodgett (LB) film suffer from the same disadvantages.

To overcome this, direct initiation of a polymer chain from a surface can be applied, which is expected to lead to higher surface grafting densities, because monomers can more easily diffuse toward the reactive center, whereas grafting or selective adsorption of polymers is limited by steric and entropic forces.

Controlled/"living" radical polymerization (CLRP) techniques emerged in recent years offer potential

use in surface grafting.<sup>1</sup> As applied to surface-initiated graft polymerization, it has the overwhelming advantage over other surface grafting techniques in that it allows grafting of homo- and copolymers of controlled structures with an extremely high graft density. The surface-initiated controlled/"living" radical polymerization (SI-CLRP) techniques have been lucubrated in the last decade and have successfully used for the graft polymerization from the surfaces of nanosurfaces,<sup>2,3</sup> fibers,<sup>4–7</sup> particles,<sup>8–15</sup> and films,<sup>16–19</sup> etc.

Nowadays, The SI-CLRP techniques are receiving increasing attention as a method for surface functionalization.<sup>20</sup> Bicak and coworkers had reported the preparation of the selective mercury adsorbents based on polystyrene beads<sup>21,22</sup> by surface-initiated atom-transfer radical polymerization (SI-ATRP) technique. Some porous membranes had also been surface functionalized by the SI-ATRP technique.<sup>23,24</sup> We had prepared polyacrylamide-grafted attapulgite nanofibrillar clay by the SI-ATRP technique and its adsorption properties toward Hg(II) and dyes were studied.<sup>25</sup>

The poly(vinyl chloride) (PVC) had been successfully used as the supports for the ion-exchange and adsorption resins,<sup>26</sup> sensors,<sup>27</sup> antithrombogenicity utilization,<sup>28</sup> microfiltration membranes,<sup>29</sup> medical applications,<sup>30,31</sup> and so on because of their surface active C—Cl groups. Poly(hydroxyethyl acrylate) (PHEA) had been grafted from the surfaces of crosslinked

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PVC beads with their surface labile chlorines as initiation sites, using copper-mediated SI-ATRP methodology. The ester groups of the poly(hydroxyethyl acrylate) grafted crosslinked PVC beads (PHEA-PVC) were then hydrolyzed to yield carboxyl groups. Then, the bare PVC beads, PHEA-PVC beads, and the hydrolyzed product, poly(acrylic acid) grafted crosslinked PVC beads (PAA-PVC), were used for the extraction of heavy metal ions such as Cu(II), Hg(II), Zn(II), and Cd(II) in weak acidic aqueous solution.<sup>32</sup>

In the present work, the crosslinked PVC beads were modified with diethyldithiocarbamyl groups and the diethyldithiocarbamyl crosslinked PVC beads (DEDTC-PVC) was used as a macroiniferter for the SI-CLRP of acrylamide and the Hg(II) adsorption property of the products, polyacrylamide grafted crosslinked PVC beads (PAM-PVC), was investigated preliminarily.

## EXPERIMENTAL

### Materials

The crosslinked PVC beads, products of flash polymerization with uncontrolled acceleration of the polymerization rate, used were purchased from Yanguoxia Chemical Factory, Gansu, China, and used after being washed with ethanol, and then being dried at 80°C for 24 h. Sodium *N,N*-diethyl dithiocarbamate was analytical grade reagent from Shanghai Chemical Reagent Co., Tianjin, China. Acrylamide (AM) (Tianjin Chemical Reagent Co.,

Tianjin, China) is analytical reagent grade and used as received. Ethanol, toluene, and all other solvents used are all analytical reagent grade. Distilled water was used throughout.

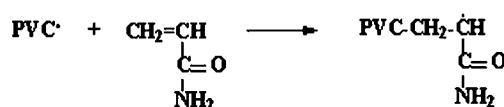
### Preparation of the macroiniferters

The macroiniferters, diethyldithiocarbamyl crosslinked poly(vinyl chloride) beads (DEDTC-PVC) were prepared by the reaction of the surface C—Cl groups with sodium *N,N*-diethyl dithiocarbamate. In a 250-mL, three-necked flask equipped with a motor stirrer, a reflux condenser, and a temperature controller were placed PVC (3 g), ethanol (120 mL), and sodium *N,N*-diethyl dithiocarbamate (0.5 g, about 2.22 mmol). The reaction continued under stirring for 6 h at 60°C. After the reacting mixture cooled to the room temperature, the polymer beads were filtered and washed with ethanol for many times to remove the remained sodium salt. Then, the macroiniferters were dried at 40°C in vacuum.

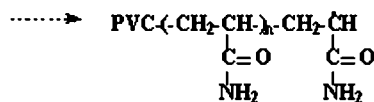
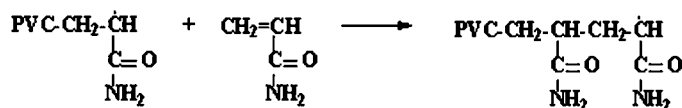
### UV-irradiated polymerization

The surface-initiated controlled/"living" radical polymerization of acrylamide from DEDTC-PVCs was carried out at ambient temperature (20°C) using a 300 W UV lamp (qe6,  $\lambda = 365$  nm, Osram Corp., Germany) at a distance of 10 cm. 3.0 g DEDTC-PVCs and 15.0 g acrylamide were charged in 60.0 mL water and the mixture was placed under the UV lamp for irradiation with mild electromagnetic stirring. After polymerization for a given time, the polyacrylamide

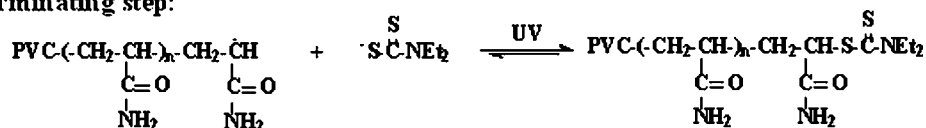
#### Initiating step:



#### Propagating step:



#### Terminating step:



Scheme 1 The mechanism of surface-initiated photopolymerization.

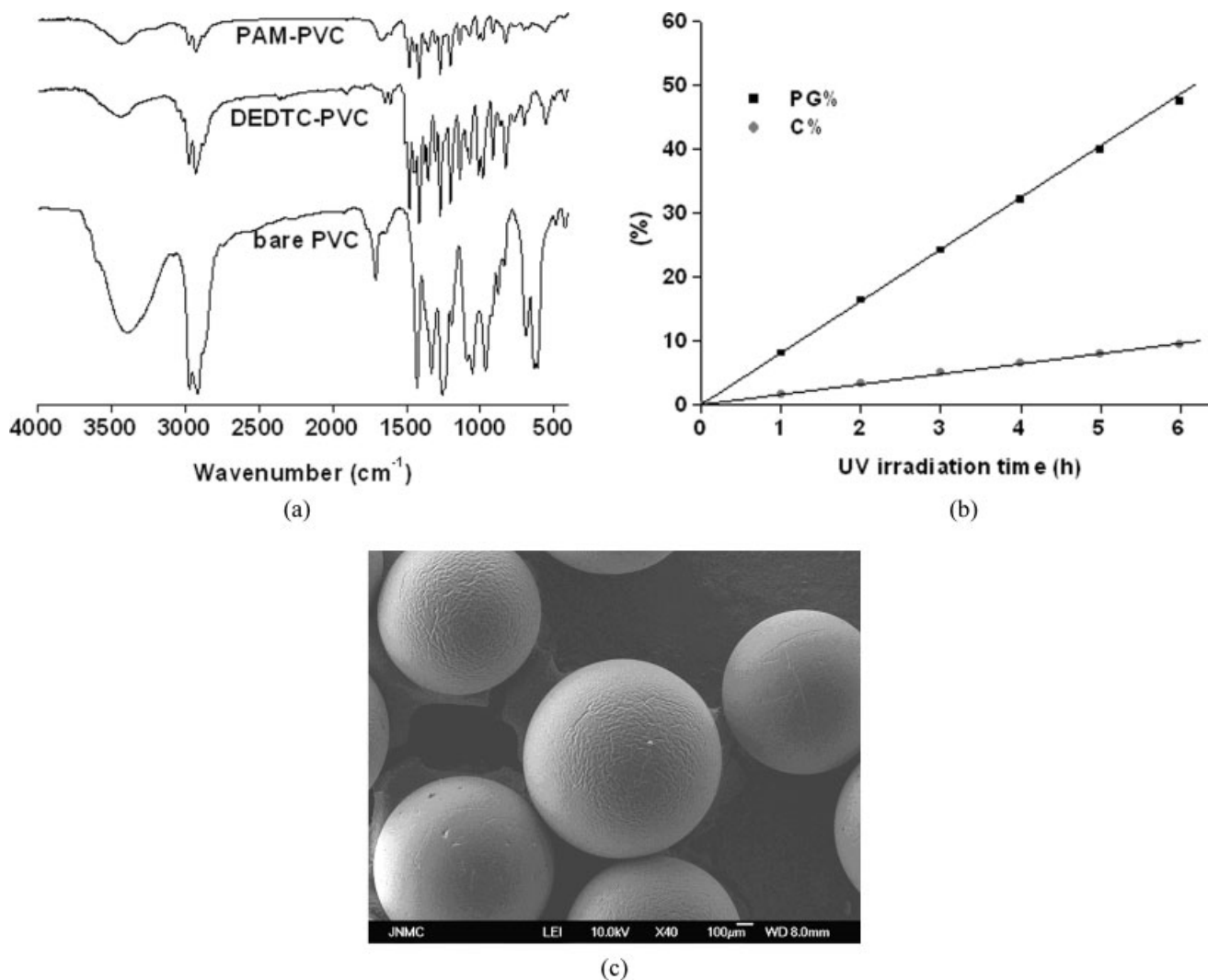


Figure 1 FTIR spectra of (a) bare PVC, (b) DEDTC-PVC, and (c) PAM-PVC.

grafted crosslinked poly(vinyl chloride) powder (PAM-PVC) was taken out and extracted with water, dried in vacuum at 40°C. The mechanism of the surface-initiated (SI) controlled/"living" radical polymerization of acrylamide from DEDTC-PVC was illustrated in Scheme 1.

#### Analyses and characterizations

Elemental analysis (EA) of C and H was performed on Elementar vario EL instrument. Fourier transform infrared (FTIR) was performed using a Bio-RAD FTS-165 spectrometer by KBr disk. The surface morphologies of the polymer beads and powders were characterized with a Philips XL-20 scanning electron microscope (SEM) (Philips Co., Netherlands). The grafting parameters were estimated from the results of elemental analyses. The conversion of the monomer (C%) and the percentage of grafting

(PG%) were calculated according to the following relationships:

$$C\% = \text{PAM grafted (g)} / \text{monomer used (g)} \times 100\%$$

$$PG\% = \text{PAM grafted (g)} / \text{PVC charged (g)} \times 100\%$$

#### Adsorption of Hg(II) ion

The uptake capacity and the loading rate of the PAM-PVC powders were determined preliminary as follows: 1.0 g powders were stirred in 30 mL aqueous solution of 1.0 mg/mL Hg (II) ion in HCl media (pH = 5.0). Then the mixture was shaken for 1 h at room temperature. Then the supernatant solutions were taken out for the ICP-OES (PerkinElmer ICP/6500 inductively coupled plasma optical emission spectrometer, RF power supply: 1100 w, Ar plasma gas flow 14.0 L min<sup>-1</sup>, Ar auxiliary gas flow 0.5 L min<sup>-1</sup>,

Ar nebulizer gas flow  $1.0 \text{ L min}^{-1}$ , viewing height 11 mm; Detection line: Hg 194.2 nm) determination.

## RESULTS AND DISCUSSION

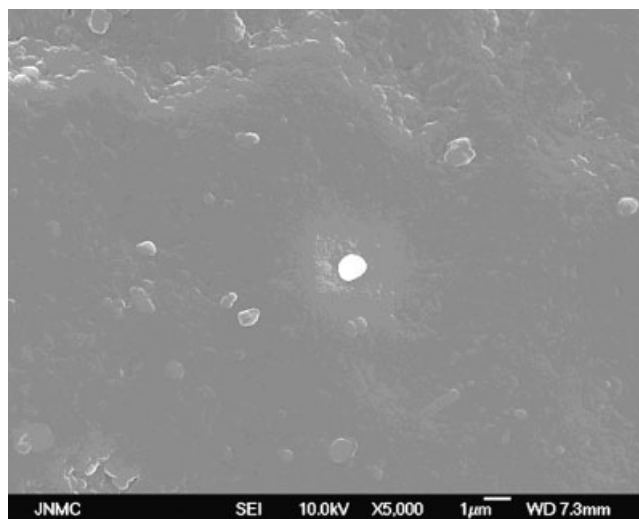
### Macroinitiators

There were four facts that could show the occurrence of the substitution reaction of the surface C—Cl groups with sodium *N,N*-diethyl dithiocarbamate. Sodium chloride was precipitated during the reaction. The weight of product increased after the reaction, owing to the change of substitution on the PVC side chain. The diethyldithiocarbamyl group functionalized crosslinked PVC beads were fall to pieces in the polymerizing condition but the beads without surface modification were intact in toluene system with the same gentle electromagnetic stirring under UV irradiation. The carbon element content was decreased from 72% to 65% and a 4% of nitrogen element content was found after the reaction. The photoiniferter content could be calculated to be  $2.6 \text{ mmol/g}$ , from the elemental analysis results. The characteristic peak of diethyldithiocarbamyl at  $1647 \text{ cm}^{-1}$  appeared in the IR spectrum of macroiniferter DEDTC-PVC (Fig. 1).

### Surface-initiated controlled/"living" radical polymerization

FTIR spectrum of the extracted polymer, which confirmed that the resulting product was grafted polymer, is shown in Figure 1. Compared with the bare PVC beads, whose characteristic peak is at  $1258 \text{ cm}^{-1}$ , characteristic peaks were observed at about  $1650$ ,  $3175$ , and  $3300 \text{ cm}^{-1}$  represented polyacrylamide. The *N,N*-diethyldithiocarbamate group was sensitive to UV irradiation. In DEDTC-PVC, the photolysis of the *N,N*-diethyldithiocarbamate group can be seen in the form of macromolecular carbon radical ( $\text{PVC}^{\cdot}$  with higher initiating activity and the small molecular sulfur radical ( $^{\cdot}\text{SC(S)NEt}_2$ ) with lower initiating activity. And then the macromolecular carbon radical initiated the radical polymerization of acrylamide; the  $\text{Et}_2\text{NSCS}^{\cdot}$  radical mainly reacted with growing radicals  $\text{RM}_n^{\cdot}$  to form dormant covalent species, which can again photochemically dissociate.<sup>33–36</sup>

According to the above mechanism of polymerization with DEDTC-PVC photoiniferter, the PVC beads bearing *N,N*-diethyldithiocarbamyl structure can serve as a photoiniferter and the polymerization should display characteristics of a "living" radical polymerization. The graft copolymerization was carried out in water as a solvent. The bare DEDTC-PVC beads were natant and did not immerge in water. They were immersed into water within 2 h of the reaction.

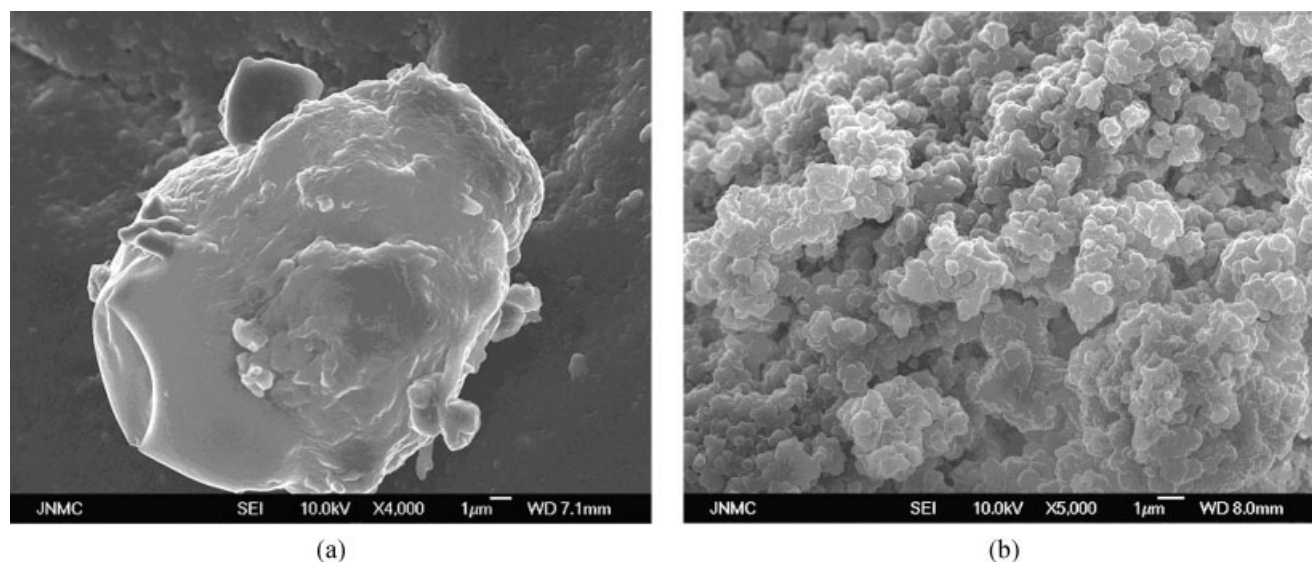


**Figure 2** Photopolymerization of acrylamide from the macroiniferters.

This formulation enabled us to perform SI-CLRP under entirely heterogeneous conditions. The percentage of grafting (PG%) and the conversion of acrylamide with different UV irradiation time were calculated from the elemental analyses results shown in Figure 2. They all increased linear with increasing of the polymerization time and reached 47.6% with a conversion of acrylamide of 9.52% after a UV irradiation time of 6 h. Both of them are nearly a straight line. It was resulted from the low modification density of *N,N*-diethyldithiocarbamyl groups on the surfaces of the photoiniferter and there would be less effect of the space hindrance in the surface-initiated polymerization of acrylamide.

### Morphological analysis

It is noteworthy that the PVC beads with the diameter at millimeter scale [Fig. 3(a)] had broken into pieces at micron scale [Fig. 3(b)] after the photopolymerization of acrylamide from the macroiniferters. For the same system as the photopolymerization except that no acrylamide was added, the DEDTC-PVC photoiniferter beads retained their spherical shape even after being irradiated with UV for more than 10 h. Furthermore, the bare PVC beads also had not any change after being irradiated with UV for more than 10 h in the same mixture of water and acrylamide. It indicated that acrylamide had been grafted from the surfaces of the PVC beads and the grafted polyacrylamide enhanced the water adsorption of the PVC supports because of the polyacrylamide could dissolve in water. So the polyacrylamide grafted crosslinked PVC beads (PAM-PVC) adsorbed a mass of water and swelled. Then, they broke into pieces even under the mild electromagnetic stirring.



**Figure 3** SEM images of (a) the bare PVC beads; and (b) the PAM-PVC powders after 6 h of photopolymerization.

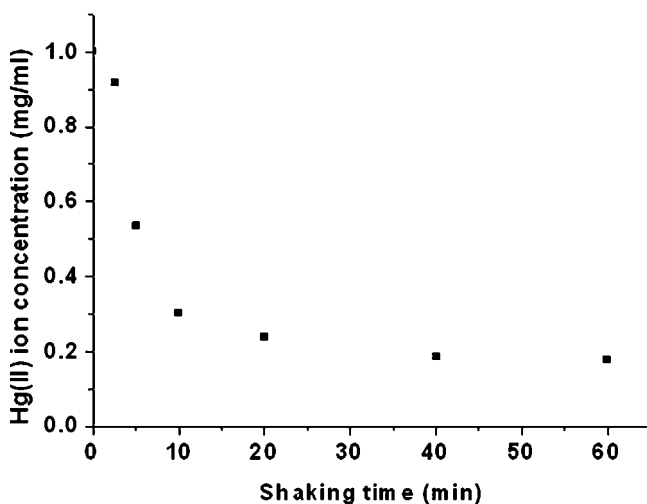
It was also found in Figure 3 that the surfaces of the polyacrylamide grafted crosslinked PVC beads (PAM-PVC) became unshaped after the photopolymerization. This also indicated that the polyacrylamide had been successfully grafted from the surfaces of the PVC beads with the proposed macroiniferter technique.

### Adsorption of Hg(II) ion

The carbonamide functional groups on the flexible polyacrylamide graft chains should offer the opportunity for rapid interaction with aqueous Hg(II) solution to form chelate complex, as in the case for low molecular weight amide compounds. Binding can occur, in principle, either by formation of mono-

amido- or diamido-Hg structures, which provide a means of capturing Hg(II) ions from aqueous solution. Aqueous solutions of HgCl<sub>2</sub> were used in the Hg(II) sorption experiments. The sorption capacity of the PAM-PVC films was assessed by analysis of the excess Hg(II) ions in the supernatant solutions.

Batch kinetic sorption experiments from dilute (1.0 mg/mL) Hg(II) solutions indicated the relatively fast binding of Hg (Fig. 4). The uptake obeys second-order kinetics as in the case of many metal complexation involving solid surfaces. After 1 h period of shaking in the Hg(II) solution, sorption equilibrium was achieved and the sorption capacity was found to be 0.123 mmol/g. Furthermore, the adsorbed Hg(II) ions could be eluted by being immersed in 0.1M HCl solution. The material presented here is regenerable and has the advantage of mobility of the graft chains in Hg(II) ion removal from aqueous solutions.



**Figure 4** Plot of solution concentration of Hg(II) ion in contact with PAM-PVC powders as a function of time.

### CONCLUSIONS

The diethyldithiocarbamyl crosslinked poly(vinyl chloride) beads (DEDTC-PVC) were prepared by the reaction of the surface C—Cl groups with sodium *N,N*-diethyl dithiocarbamate. It was used as macroiniferters for the photopolymerization of acrylamide from the surfaces of the PVC beads. The conversion of the monomer (C%) and the percentage of grafting (PG%) resulted in a high value in a short time, which means that the DEDTC-PVC could initiate the polymerization efficiently. The product, polyacrylamide grafted crosslinked PVC beads (PAM-PVC), was found to be good adsorbent for Hg(II) ion removal from aqueous solutions.

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