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# Poly(*n*-butyl Acrylate) Grafted Cross-linked Poly(vinyl Chloride) Beads via Surface-initiated Controlled/“Living” Radical Polymerization and its Adsorption Properties for Organic Solvents

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Poly(*n*-butyl acrylate) grafted cross-linked poly(vinyl chloride) beads (PBA-PVC) were prepared by the surface-initiated controlled/“living” radical polymerization (SI-CLRP) methodology on cross-linked poly(vinyl chloride) beads that had been surface modified with diethyldithiocarbamyl groups under UV irradiation. The macroinitiators, diethyldithiocarbamyl surface modified cross-linked 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 polymerization time and reached 53.3% after 6 h UV irradiation. The beaded polymer with a poly(*n*-butyl acrylate) surface shell were characterized with Fourier transform infrared (FTIR) and scanning electron microscope (SEM). The absorbencies of the polymer beads towards organic solvents such as acetone, ethanol, toluene, and chloroform were enhanced markedly after the SI-CLRP of *n*-butyl acrylate.

**Keywords:** poly(*n*-butyl acrylate); cross-linked poly(vinyl chloride) beads; surface-initiated controlled/“living” radical polymerization; macro-iniferters; adsorption properties

## 1 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, however, this 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, this 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, which have emerged in recent years, offer potential use in surface grafting (1). 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 developed in the last decade and have been successfully used for the graft polymerization from the surfaces of nanosurfaces (2, 3), fibers (4–7), particles (8–15), films (16–19), etc.

Nowadays, the SI-CLRP techniques are receiving increasing attention as a method for surface functionalization (20). Bicak et al. reported the preparation of selective mercury adsorbents based on polystyrene beads (21, 22) by surface-initiated atom transfer radical polymerization (SI-ATRP) technique. Some porous membranes have also been surface functionalized by the SI-ATRP technique (23, 24).

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Poly(vinyl chloride) had been successfully used as supports for ion-exchange and adsorption resins (25), sensors (26), antithrombogenicity utilization (27), microfiltration membranes (28), medical applications (29, 30), etc., because of its surface active C-Cl groups. In the present work, cross-linked poly(vinyl chloride) beads (PVC) were surface modified with diethyldithiocarbamyl groups and the diethyldithiocarbamyl cross-linked poly(vinyl chloride) beads (DEDTC-PVC) were then used as macro-initiators for the SI-CLRP of n-butyl acrylate (BA).

## 2 Experimental

### 2.1 Materials

The cross-linked PVC beads used (about 1 mm diameter) were purchased from Yanguoxia Chemical Factory, Gansu, China and used after being washed with ethanol, and dried at 80°C for 24 h. Sodium N,N-diethyl dithiocarbamate was an analytical grade reagent. n-Butyl acrylate (BA) (Tianjin Chemical Reagent Co., Tianjin, China) was of analytical reagent grade, washed twice with an aqueous solution of sodium hydroxide (5%), twice with distilled water, dried with anhydrous magnesium sulfate overnight, and then distilled over calcium hydride under vacuum. Ethanol, toluene, and all other solvents used were of analytical reagent grade.

### 2.2 Preparation of the Macroinitiators

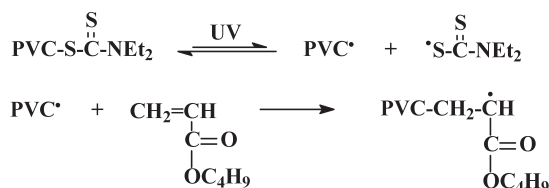
The macroinitiator, diethyldithiocarbamyl surface modified cross-linked poly(vinyl chloride) beads (DEDTC-PVC)

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 electromagnetic stirrer, reflux condenser and temperature controller, were placed PVC (3 g), ethanol (120 mL), and sodium N,N-diethyl dithiocarbamate (0.5 g). The reaction continued under stirring for 6 h at 60°C. After the reacting mixture cooled to room temperature, the polymer beads were filtered and washed with ethanol numerous times to remove the remaining sodium salt. Then, the macroinitiators were dried at 40°C in vacuum.

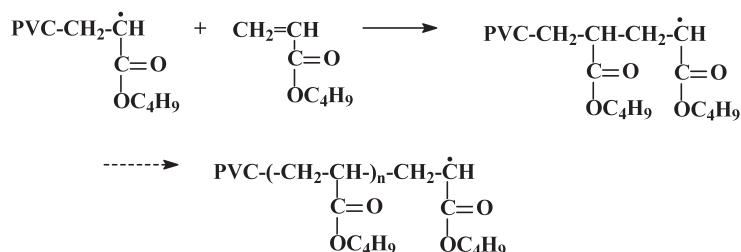
### 2.3 UV Irradiated Polymerization

The surface-initiated controlled/“living” radical polymerization of n-butyl acrylate on the DEDTC-PVCs was carried out at ambient temperature (20°C) using a 300 W UV lamp (qe6,  $\lambda = 365$  nm, Osram Corporation, Germany) at a distance of 10 cm. 3.0 g of DEDTC-PVCs was dispersed in a 30.0 mL mixture of toluene and n-butyl acrylate (vol. ratio: 1:1) and the mixture was placed under the UV lamp for irradiation with mild electromagnetic stirring in N<sub>2</sub> atmosphere. After polymerization for varying times from 1 to 6 h, the poly(n-butyl acrylate) grafted cross-linked poly(vinyl chloride) powder (PBA-PVC) was taken out and extracted with toluene and dried in vacuum at 40°C. The mechanism of the surface-initiated (SI) controlled/“living” radical polymerization of n-butyl acrylate from DEDTC-PVCs is illustrated in Sch. 1.

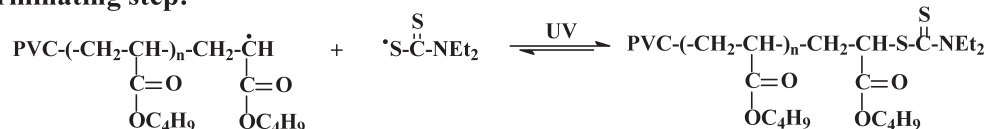
#### Initiating step:



#### Propagating step:



#### Terminating step:



Sch. 1. The mechanism of surface-initiated photopolymerization.

### 2.3 Analyses and Characterizations

Elemental analysis (EA) of C and H was performed on a Elementar vario EL instrument (ELEMENTAR Company, Germany). Fourier transform infrared (FTIR) was performed using a Bio-RAD FTS-165 spectrometer (Japan Bio-Rad Laboratories Company, Japan) with a 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:

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

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

### 2.4 Adsorption of Organic Solvents

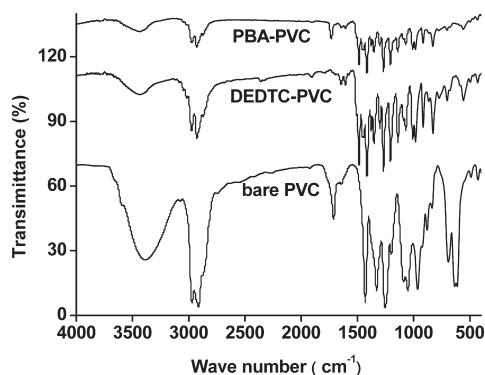
Accurately weighed 1.0 g samples of bare PVC or PBA-PVC were immersed in various organic solvents (acetone, ethanol, toluene, and chloroform) in a sealed flask with shaking for 30 min at room temperature. Then the organic solvent-adsorbed beads or powders were filtered and weighed. The organic solvent absorption ratio (OSAR%) was calculated by the gravimetric method with the following relationships:

$$\text{OSAR}\% = \left( \frac{\text{organic solvent-adsorbed resin (g)} - \text{PBA-PVC (g)}}{\text{PBA-PVC (g)}} \right) \times 100\%$$

## 3 Results and Discussion

### 3.1 Macro-initiators

There were four observations that showed the occurrence of the substitution reaction of the surface C-Cl groups with sodium *N,N*-diethyl dithiocarbamate. 1) Sodium chloride was precipitated during the reaction; 2) The weight of product increased after the reaction, owing to the change of



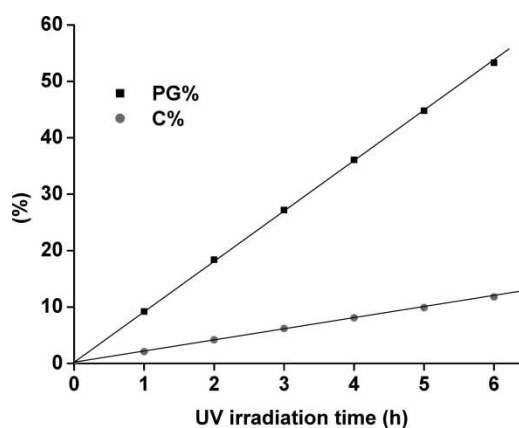
**Fig. 1.** FTIR spectra of a) bare PVC, b) macro-initiators, and c) PBA-PVC.

substitution on the PVC; 3) The cross-linked PVC beads fell to pieces during polymerization in toluene, but the beads without surface modification were intact in toluene with the same gentle electromagnetic stirring under UV irradiation; 4) The carbon element content decreased from 72% to 65% and a 4% of nitrogen element content was found after the reaction. The photo-initiator content could be calculated to be 2.6 m mol/g, from the elemental analyses results. The characteristic peak of the diethyldithiocarbamyl group at  $1647 \text{ cm}^{-1}$  appeared in the IR spectrum of macroinitiator (Fig. 1).

### 3.2 Surface-initiated Controlled/“Living” Radical Polymerization

Fourier transform infrared (FTIR) spectrum of the extracted polymer, which confirmed that the resulting product was grafted polymer, is shown in Fig. 1. The cross-linked PVC beads used were products of the “runaway” polymerization. The adsorption peak at about  $1700 \text{ cm}^{-1}$  in the PVC beads before the grafting is assigned to the carbonyl groups formed in the “runaway” polymerization (31). The absorption peak at  $615 \text{ cm}^{-1}$ , which is the characteristic absorption of the C-Cl bond vibration for PVC, was found to be reduced markedly after the surface modification with the diethyldithiocarbamyl group and the SI-CLRP of *n*-butyl acrylate. After the SI-CLRP, the characteristic peak representing poly(*n*-butyl acrylate) appeared at  $1732 \text{ cm}^{-1}$ . This indicated that the poly(*n*-butyl acrylate) chains had been successfully grafted on the cross-linked PVC beads.

The *N,N*-diethyl dithiocarbamate group was sensitive to UV irradiation. In DEDTC-PVCs, the photolysis of the *N,N*-diethyl dithiocarbamate group results in the formation of macromolecular carbon radicals ( $\text{PVC}^\bullet$ ) with higher initiating activity and the small molecular sulfur radical ( $^\bullet\text{SC(S)NEt}_2$ ) with lower initiating activity. The macromolecular carbon radical initiated the radical polymerization of *n*-butyl acrylate, the  $\text{Et}_2\text{NSCS}^\bullet$  radical mainly reacted with



**Fig. 2.** Photopolymerization of *n*-butyl acrylate from the macro-initiators.

growing radicals  $RMn^{\bullet}$  to form dormant covalent species, which can again photochemically dissociate (32, 33).

According to the above mechanism of polymerization with DEDTC-PVCs photoinitiator, the PVC beads bearing *N,N*-diethyl dithiocarbamyl structure can serve as a photoinitiator

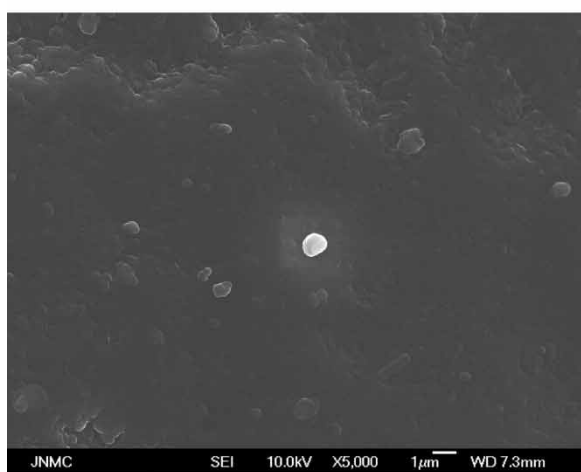
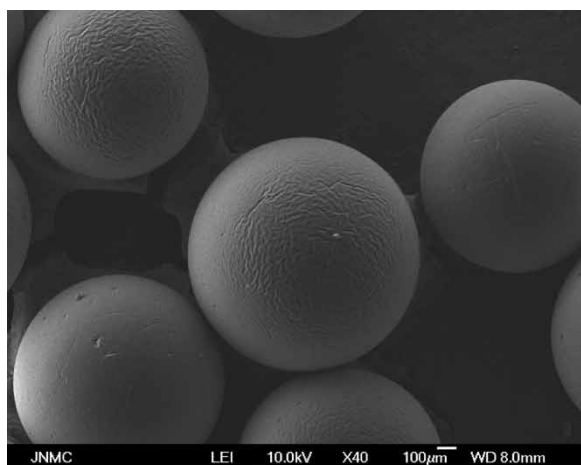
and the polymerization should display the characteristics of a living radical polymerization. The percentage of grafting (PG%) and the conversion of *n*-butyl acrylate with different UV irradiation times were calculated from the elemental analyses results and is shown in Fig. 2. They increased linearly with increasing of the polymerization time and PG% reached 53.3% with a conversion of *n*-butyl acrylate of about 12% after a UV irradiation time of 6 hrs. Both of them are nearly straight lines. This resulted from the low density of *N,N*-diethyl dithiocarbamyl groups on the surfaces of the photo-initiator, there would be less effect of space hindrance in the surface-initiated polymerization of *n*-butyl acrylate.

### 3.3 Morphological Analysis

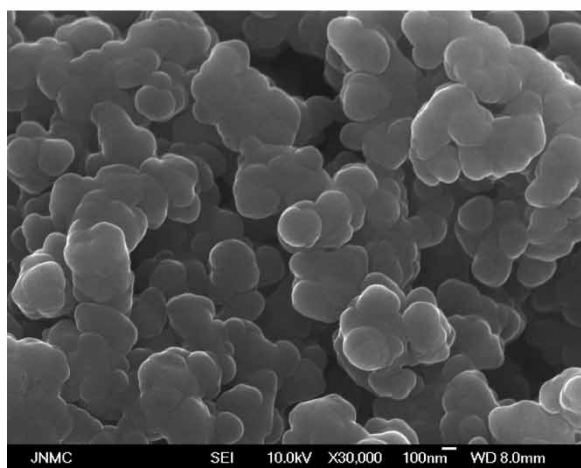
It is noteworthy that the PVC beads, with a diameter on the millimeter scale Fig. 3a, had broken into pieces on the micron scale Fig. 3b after the photopolymerization of *n*-butyl acrylate from the macro-initiators. For the same system as the photopolymerization, except that no *n*-butyl acrylate was added, the DEDTC-PVC photo-initiferter beads retained their spherical shape even after being irradiated with UV for more than 10 h. Furthermore, the bare PVC beads also had no change after being irradiated with UV for more than 10 h in the same mixture of toluene and *n*-butyl acrylate. This indicated that *n*-butyl acrylate had been grafted on the surfaces of the PVC beads and the grafted poly(*n*-butyl acrylate) enhanced the solvent adsorption of the PVC supports (34, 35). Thus, the poly(*n*-butyl acrylate) grafted cross-linked poly(vinyl chloride) beads (PBA-PVC) adsorbed a mass of the solvent and monomer and were swollen. Then they broke into pieces even under the mild electromagnetic stirring. The PBA-PVC particle diameters are near the primary particles of PVC (36). The PBA grafted and the larger surface area of the PBA-PVC particles might show higher organic solvent absorption ratio (OSAR%) than the bare PVC beads.

### 3.4 Adsorption of Organic Solvents

The phenomenon that the poly(*n*-butyl acrylate) grafted cross-linked poly(vinyl chloride) beads (PBA-PVC)

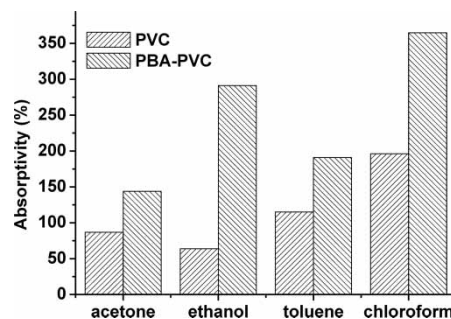


(a)



(b)

**Fig. 3.** SEM images of (a) the bare PVC beads, and (b) the PBA-PVC powders.



**Fig. 4.** The organic solvent absorption ratios of the bare PVC beads and the PBA-PVC powders.

adsorbed a mass of the solvent was found following the photopolymerization process. Cross-linked polymeric materials with butyl side groups are widely used as oil absorbing resins (34, 35). So the adsorption of organic solvents by the poly(n-butyl acrylate) grafted cross-linked poly(vinyl chloride) beads (PBA-PVC) were initially investigated. The results are given in Fig. 4. The PBA-PVC powders had a much higher organic solvent absorption ratio (OSAR%) than the bare PVC beads. It is expected that the products could be used as adsorbents for organic solvents in air or water.

#### 4 Conclusions

The diethyldithiocarbamyl surface modified cross-linked poly(vinyl chloride) beads (DEDTC-PVC) were prepared by the reaction of the surface C-Cl groups on cross-linked beads with sodium *N,N*-diethyl dithiocarbamate. These were then used as macro-initiators for the photopolymerization of n-butyl acrylate on the surfaces of the PVC beads. The conversion of the monomer (C%) and the percentage of grafting (PG%) were large in a short time, which means that the DEDTC-PVC could initiate the polymerization efficiently. The products, poly(n-butyl acrylate) grafted cross-linked poly(vinyl chloride) beads (PBA-PVC), had much higher organic solvent absorption ratio (OSAR%) than the bare PVC beads. It is expected that the products could be used as adsorbents for organic solvents in environmental-cleaning.

#### 5 Acknowledgments

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