

Photografting of PVC Containing *N,N*-diethyldithiocarbamate Groups with Vinyl Monomers

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ABSTRACT: Poly(vinyl chloride) (PVC) with pendent *N,N*-diethyldithiocarbamate groups (PVC-SR) was prepared through the reaction of PVC with sodium *N,N*-diethyldithiocarbamate (NaSR) in butanone and used as a photoinitiator for the grafting polymerization of three vinyl monomers [styrene (St), methyl methacrylate (MMA), and acrylamide (Am)]. The effects of ultraviolet (UV) irradiation time, PVC-SR amount, and the monomer amount on grafting and grafting efficiency were investigated. The results showed that PVC-SR could initiate the polymerization of three vinyl monomers effectively and obtained crosslinked copolymers. The grafting and grafting efficiency of styrene and methyl methacrylate were higher than those of acrylamide. The polymerization activity of three monomers was acrylamide > methyl methacrylate > styrene. By analyzing the UV spectrum of PVC-SR with a different irradiation time, it was confirmed that PVC-SR was dissociated mainly into macromolecular the sulfur radical PVC-S· and the small molecular carbon radical ·C(S)N(C₂H₅)₂; the grafting polymerization mechanism was discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2569–2574, 2000

Key words: poly(vinyl chloride); grafting; ultraviolet irradiation; functional polymer

INTRODUCTION

Grafting is one of the most effective ways to improve the comprehensive properties of poly(vinyl chloride) (PVC) because the copolymer combined the properties of homopolymers. PVC could be grafted with vinyl monomers, such as styrene and acrylonitrile by anionic, cationic, radical, and irradiation polymerization.^{1–4} Among them, irradiation polymerization was widely used as it was easily conducted and controlled. The commonly used γ -ray irradiation could realize the graft po-

lymerization under a much high dose; however, it usually breaks the macromolecular chain and decreases the properties of copolymer correspondingly. Compared with γ -ray irradiation polymerization, UV irradiation polymerization overcomes the shortcoming and attracts much more attention.

To realize the ultraviolet (UV) irradiation polymerization, the photosensitive groups on the polymer chain was critical. The *N,N*-diethyldithiocarbamate group was UV-sensitive. Small molecular compounds containing *N,N*-diethyldithiocarbamate groups had the properties of bioactivity,⁵ accelerating the crosslinking of rubber and initiating the polymerization of vinyl monomers under UV irradiation or heating.^{6–8} By introducing the *N,N*-diethyldithiocarbamate groups

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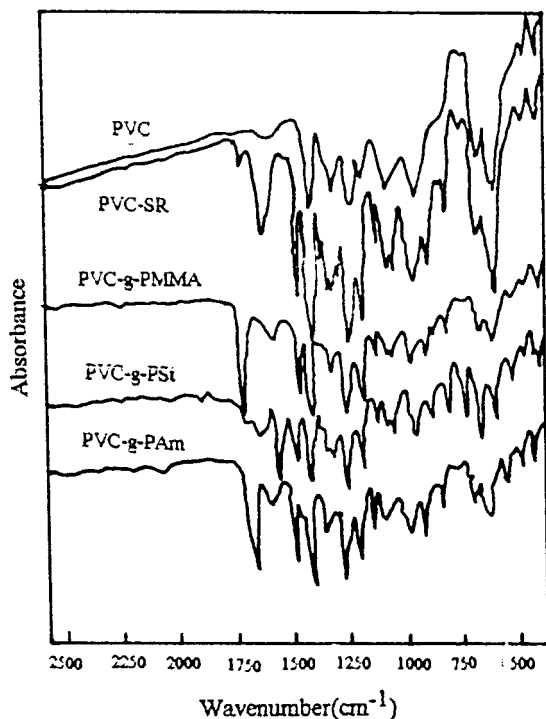


Figure 1 IR spectrum of PVC, PVC-SR, and grafting products: PVC, commercial PPVC reprecipitated from the THF-EtOH system; PVC-SR, PVC with pendent *N,N*-diethyldithiocarbamate groups; grafting products, extracted products.

into polymer chain, the functional polymer thus obtained not only had the properties of the group itself but also provided the way for further modification of the polymer. In our previous article,⁹ PVC with *N,N*-diethyldithiocarbamate groups was used to enhance the crosslinking reactions of PVC and the PVC-NBR blend under UV irradiation and obtained a high degree of gel product. In this article, we used it as a macromolecular photoinitiator to initiate the grafting polymerization of styrene, methyl methacrylate, and acrylamide. The results obtained are described and discussed.

EXPERIMENTAL

Materials

PVC (DP = 700; porous type) was supplied by Qilu Petrochemical Co., China. Sodium *N,N*-diethyldithiocarbamate (NaSR) was from Shanghai Chemical Co., China. The solvents and precipitants used were all analytically pure without further purification. The styrene, methyl methacry-

late, and acrylamide monomers were purified by vacuum distilled before using.

Preparation of PVC-SR

PVC-SR was synthesized from the reaction of PVC with NaSR. In a 250-mL, three-necked flask equipped with a motor stirrer, a reflux condenser and a temperature controller were placed PVC (3 g), butanone (120 mL), and NaSR (0.35 g). The reaction continued under stirring for 6 h at 60°C. The solution was then poured into a large amount of ethanol. The precipitated products were purified by reprecipitating from the butanone-ethanol system and dried under vacuum.

Grafting Polymerization

The required amount of PVC-SR, monomer, and THF were charged into Pyrex glass tubes closed with a rubber stopper and then replaced with nitrogen. Grafting polymerization were carried out under irradiation from a high pressure mercury lamp (250 W) at a distance of 18 cm for a given time; the ambient temperature was 36°C. The content of the tube was then poured into a large amount of methanol to isolate the polymer and then dried. The polymer obtained were extracted with suitable solvents to separate unreacted PVC-SR and homopolymer, that is, cyclohexane and THF for PVC-g-PS, acetone, and THF for PVC-g-PMMA, water, and THF for PVC-g-PAm.

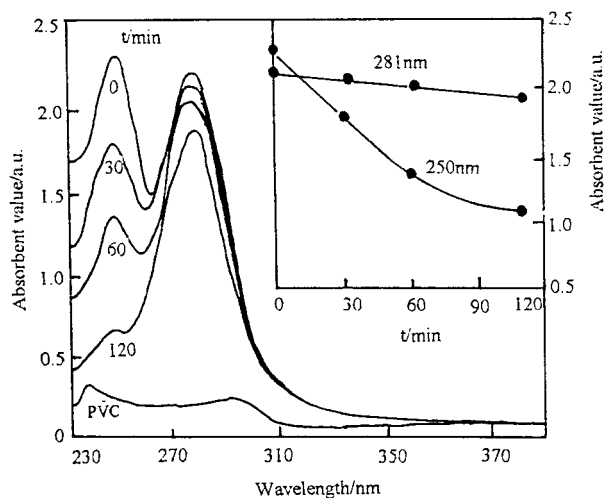


Figure 2 UV spectrum of PVC and PVC-SR with different irradiation times. The concentration of PVC-SR = 7.2×10^{-3} g/mL. The irradiation time (min) was marked on the corresponding curve.

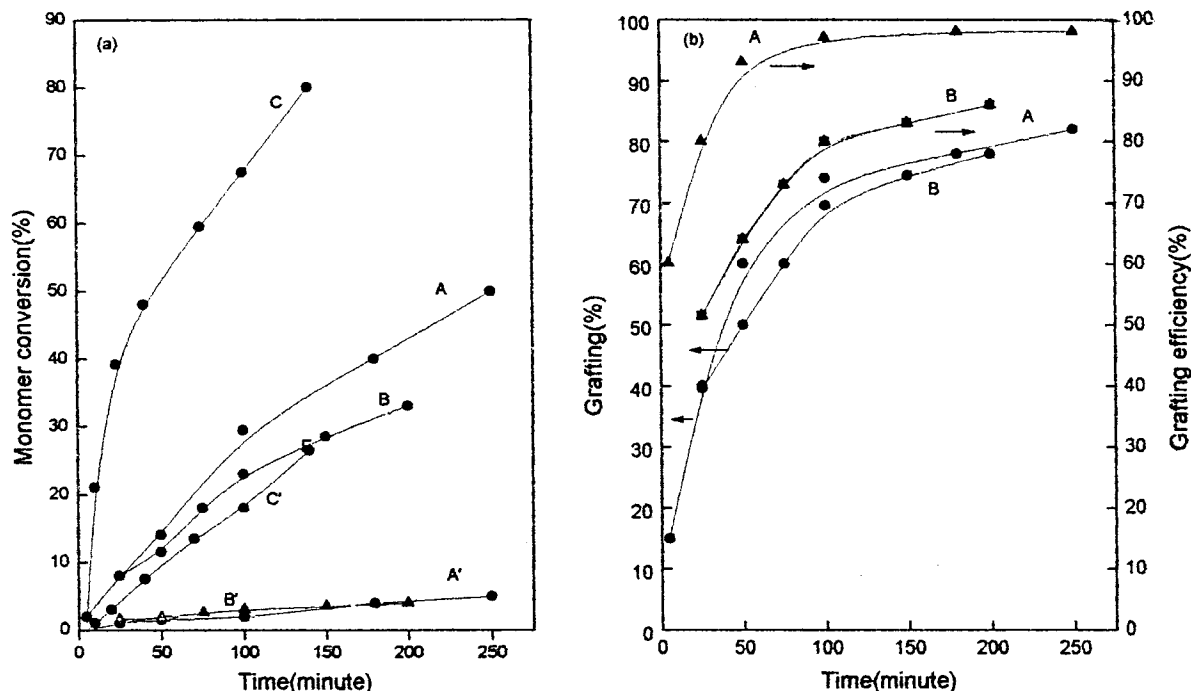


Figure 3 Effect of irradiation time on (a) the monomer conversion and (b) grafting and grafting efficiency. Content of chloride in PVC-SR, 36%; PVC-SR, 0.3 g; THF, 10 mL; methyl methacrylate, 3 mL; styrene, 2 mL; acrylamide, 2 g; ambient temperature, 36°C: (A) methyl methacrylate; (A') methyl methacrylate without PVC-SR; (B) styrene; (B') styrene without PVC-SR; (C) acrylamide; (C') acrylamide without PVC-SR.

Characterization of Products

The content of chloride in PVC-SR (Cl %, in weight) was determined by titrimetric analysis of the product of combustion by the method of ISO1158-1984; The grafting copolymer was characterized by monomer conversion (M %), grafting (G %), and grafting efficiency (GE %), as follows.

$$M (\%) = \frac{[F1(g) + F2(g) - \text{PVC-SR} (g)]}{\text{weight of monomer added} (g)} \times 100$$

$$G (\%) = \frac{[F2(g) - \text{PVC-SR} (g)]}{F2(g)} \times 100$$

$$GE (\%) = \frac{[F2(g) - \text{PVC-SR} (g)]}{[F1(g) + F2(g) - \text{PVC-SR} (g)]} \times 100$$

where $F1$ was the weight of homopolymer, and $F2$ was the insoluble part of the polymerization product.

The Fourier transform infrared (FTIR) spectrum of grafted polymers was obtained on a IFS66V FTIR recording spectrophotometer (Bruker Co.). The UV spectrum was determined

at 25°C in THF on Shimadzu UV-3100 UV-Vis-Nir recording spectrophotometer.

RESULTS AND DISCUSSION

Characterization of PVC-SR

There were four facts that could show the occurrence of the substitution reaction of PVC with NaSR, as follows:

1. Sodium chloride was precipitated during the reaction;
2. the weight of product increased after the reaction, owing to the change of substitution on the PVC side chain;
3. a characteristic peak [1644 cm^{-1} , $-\text{SC(S)N}$] appeared in the IR spectrum of PVC-SR (comparing PVC-SR with PVC in Fig. 1), and the conjugated absorbent peaks for $-\text{S}-\text{C}=\text{S}$ ($\lambda = 250 \text{ nm}$) and $\text{S}=\text{C}-\text{N}$ ($\lambda = 281 \text{ nm}$) appeared in the UV spectrum of PVC-SR [Fig. 2(a)];
4. the content of chloride in PVC-SR was

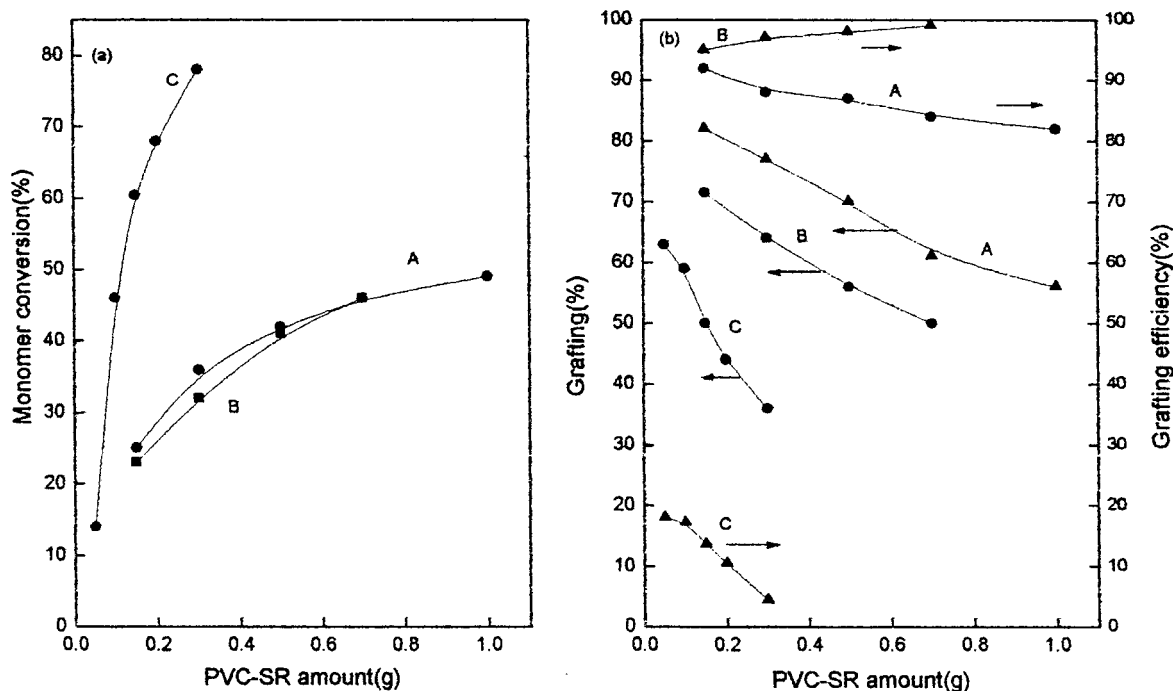


Figure 4 Effect of the PVC-SR amount on (a) the monomer conversion and (b) grafting and grafting efficiency. The content of chloride PVC-SR, 36%; THF, 10 mL; (A) methyl methacrylate, 3 mL; (B) styrene 2 mL; (C) acrylamide, 2 g, ambient temperature, 36°C.

36%, which was lower than 56.8% in unsubstituted PVC.

Effect of Polymerization Conditions on the Grafting Polymerization

PVC-SR could initiate the polymerization of three vinyl monomers. Figure 3 showed that monomer conversion of three polymerization systems containing PVC-SR were high and higher than that of systems without PVC-SR, obviously. It indicated that PVC-SR had high initiating efficiency and was an effective macromolecular photoinitiator. As the time of irradiation increased, the monomer conversion increased. To the methyl methacrylate system, when the irradiation time was beyond 50 min, the grafting and grafting efficiency changed little, while to the styrene, the grafting and grafting efficiency increased with time. The two systems had higher grafting and grafting efficiency than the acrylamide system. The fact that high grafting and grafting efficiency were obtained in a short time indicated that PVC-SR was an efficient initiator for the grafting polymerization of methyl methacrylate and styrene.

Figure 4(a) and (b) showed that with an increase in the PVC-SR amount, the monomer conversion increased while the grafting and grafting efficiency decreased. The methyl methacrylate system had higher grafting and grafting efficiency than the styrene system. One of the reasons for the decreasing of grafting and grafting efficiency was that the viscosity of systems increased when the amount of PVC-SR increased as PVC-SR was a macromolecular initiator and inhibited the grafting reaction while accelerating the homopolymerization.

The variation of monomer conversion, grafting, and grafting efficiency of three polymerization systems as a function of monomer amounts was investigated. The results are presented in Figure 5. For methyl methacrylate and acrylamide systems, the monomer conversion decreased as increase of monomer amounts, but the styrene system increased. In the methyl methacrylate and styrene systems, the grafting increased, and the grafting efficiency was high and almost unchanged; however, the grafting and grafting efficiency decreased in an acrylamide system.

As discussed above, three systems have different polymerization characters and reactivities be-

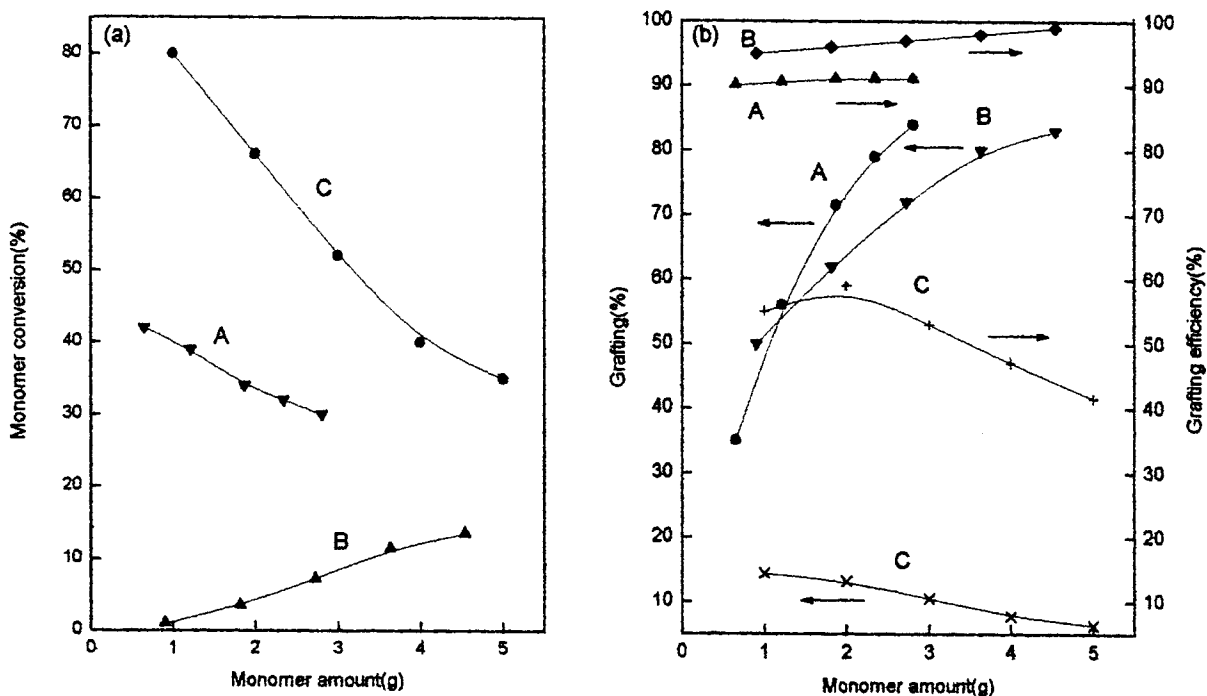


Figure 5 Effect of monomer amount on (a) the monomer conversion and (b) grafting and grafting efficiency. Content of chloride in PVC-SR, 36%; PVC-SR, 0.3 g; THF, 10 mL; ambient temperature, 36°C: (A) methyl methacrylate; (B) styrene; (C) acrylamide.

cause of the nature of three monomers. The polymerization of methyl methacrylate and styrene were homogeneous. As acrylamide and PVC-SR were soluble in THF, while polyacrylamide and grafted copolymer were insoluble in the same solvent, the polymerization of acrylamide was heterogeneous; shortly after the irradiation, the polymer had precipitated. It could be concluded from Figure 3 that the polymerization activity of three monomers was as follows: acrylamide > methyl methacrylate > styrene. Although the polymerization activity of acrylamide was highest, its grafting and grafting efficiency were lower than those of methyl methacrylate and styrene systems because of the heterophase polymerization of acrylamide.

Discussion of Mechanism of Polymerization

Infrared (IR) spectra of the extracted polymer, which confirmed that the resulting products were grafted polymers are shown in Figure 1. Compared with PVC, whose characteristic peak is at 1258 cm^{-1} , characteristic peaks were observed at 1728 , 1600 , and 1500 , and 1650 cm^{-1} and represented poly(methyl methacrylate), polystyrene, and polyacrylamide, respectively.

The *N,N*-diethyldithiocarbamate group was sensitive to UV irradiation. In PVC-SR, the photolysis of the *N,N*-diethyldithiocarbamate group can be seen in the following two ways: one was in the forming of macromolecular sulfur radical ($\text{PVC-S}\cdot$) and the small molecular carbon radical ($\cdot\text{C}(\text{S})\text{N}(\text{C}_2\text{H}_5)_2$); the other was in the forming of the macromolecular carbon radical ($\text{PVC}\cdot$) and the small molecular sulfur radical [$\cdot\text{SC}(\text{S})\text{N}(\text{C}_2\text{H}_5)_2$]. In order to obtain the information on the dissociation of PVC-SR, the UV spectrum of PVC-SR at different irradiation times were determined (Fig. 2). The two characteristic absorbent peaks of the *N,N*-diethyldithiocarbamate group changed with an increase in the irradiation time. The peak of $\lambda = 250\text{ nm}$ ($-\text{S}-\text{C}=\text{S}$) obviously decreased, and the peak of $\lambda = 281\text{ nm}$ ($\text{S}=\text{C}-\text{N}$) didn't obviously decrease. It could be considered that the photolysis of PVC-SR had occurred mainly in the $\text{S}=\text{C}$ bond of the $\text{S}-\text{C}=\text{S}$ structure, that is, forming a macromolecular sulfur radical ($\text{PVC-S}\cdot$) and a small molecular carbon radical [$\cdot\text{C}(\text{S})\text{N}(\text{C}_2\text{H}_5)_2$]. The height of the peak near 281 nm , somewhat depressed, probably resulted from the photolysis of the $\text{C}-\text{S}$ bond of the $\text{C}-\text{SC}(\text{S})\text{N}(\text{C}_2\text{H}_5)_2$ structure and from the forming of a macromolecular carbon radical ($\text{PVC}\cdot$).

and a small molecular sulfur radical [\cdot SC(S)N(C₂H₅)₂]. The carbon radical had a high initiating activity, and the sulfur radical had a high ability for combination between themselves or with the propagation chain radical; it also had the ability of chain transferring.¹⁰ So the grafting reaction was mainly from polymerization of monomers initiated by PVC \cdot and the combination of PVC-S \cdot with propagation chain radical initiated by \cdot C(S)N(C₂H₅)₂. This grafting process did not occur easily in the heterophase polymerization of acrylamide, so its grafting efficiency was low. The grafted copolymers were insoluble and did not melt under heating, which means that the grafted copolymers were crosslinked. The crosslinking reaction was mainly from the combination of macromolecular radicals (PVC \cdot , PVC-S \cdot , and the propagating chain radical). However, it is difficult to further confirm the process.

CONCLUSION

The *N,N*-diethyldithiocarbamate-substituted PVC (PVC-SR) could initiate the grafting polymerization of methyl methacrylate, styrene, and acrylamide. To the homopolymerization systems, the grafting and grafting efficiency resulted in a high value in a short time, which means that the PVC-SR could initiate the polymerization effi-

ciently. The photolysis of PVC-SR was different from that of benzyl *N,N*-diethyldithiocarbamate¹¹ (in which a benzyl and a *N,N*-diethyldithiocarbamate radical were formed). It was possible that the functional group could be used for photoinitiating the grafting polymerization of bioactive vinyl monomers on the PVC surface to increase its biocompatibility.

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