# Mechanochemical Preparation of a Novel Polymeric Photostabilizer for Poly(vinyl chloride)

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**ABSTRACT:** The preparation of a novel polymeric photostabilizer was carried out via the vibromilling of poly(vinyl chloride) (PVC) powder, a reactive light stabilizer (r-LS), and a peroxide initiator in ball-containing jars with a planetary ball mill for a certain time. The effects of the initiator content, milling time, and temperature on the grafting ratio were studied with gravimetric analysis and intrinsic viscosity measurements. Fourier transform infrared and ultraviolet–visible spectra were used to investigate the structural development of the mixture of the r-LS and PVC during vibromilling. The results showed that the r-LS was grafted onto PVC chains successfully, and the aforementioned factors had a significant effect on the grafting ratio. The optimum preparation conditions were 0.5 wt % initiator, 8 h, and 20°C. A grafting mechanism is proposed. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3079–3086, 2010

**Key words:** synthesis; poly(vinyl chloride) (PVC)

## INTRODUCTION

Poly(vinyl chloride) (PVC) materials are susceptible to degradation under the influence of ultraviolet (UV) irradiation, especially in the presence of oxygen.[1,2] When they are exposed to UV irradiation, they undergo rapid autocatalytic dehydrochlorination and consequent degradation, which causes serious changes in their color and physical and chemical properties. In general, the stability of PVC against photodegradation can be improved by melt blending with appropriate stabilizers.[3–5] However, low-molecular-weight stabilizers are easily lost from the polymer through evaporation, migration, and extraction.[6] Many efforts have been made to overcome the shortcomings.[7–10] Zhao and Dan[8] synthesized a polymerizable UV stabilizer, 2-hydroxyl-4-(3-methacryloxy-2-hydroxylpropoxy) benzophenone, through the reaction of 2,4-dihydroxybenzophenone with glycidyl methacrylate. The results of water extraction testing showed that the migration of a light stabilizer (LS) from the polymer matrix could be prevented by the anchoring of the UV stabilizer onto the polymer chain. Mohamed and Al-Magribi[9] found that the addition of an LS containing an unsaturated bond to PVC could also solve the problem of physical migration by the photografting of the stabilizer to PVC during irradiation. Essawy et al.[10] reported a hybrid high-molecular-weight stabilizer synthesized by the intercalation method. Their results showed that its excellent photostabilization in PVC was attributable to its good compatibility and low physical loss in addition to its chemical properties.

Solid mechanochemical modification of polymers has been paid more and more attention. It is an effective method for enhancing the compatibility of polymer blends and the interactions between polymers and fillers through stress-induced chemical reactions between polymers and between polymer and fillers.[11–15] Self-plasticizing aids for PVC and a core–shell impact modifier for PVC have been prepared through mechanochemical degradation and the modification of PVC in our laboratory.[16–20] Qiu and coworkers[21,22] found that maleic anhydride could be successfully grafted onto polypropylene by the ball-milling method.

In this work, the mechanochemical grafting reaction was applied to prepare a polymeric photostabilizer through the grafting of a low-basic reactive light stabilizer (r-LS) onto PVC via the process of vibratory ball milling at the ambient temperature under solvent-free conditions. The influence of the processing conditions on the grafting ratio (G%) was investigated with gravimetric analysis and intrinsic
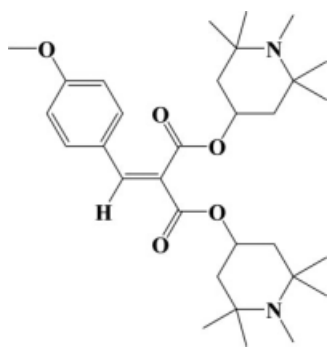
**Figure 1** Structure of the r-LS.

viscosity ([η]) measurements. A grafting mechanism is proposed on the basis of the results of Fourier transform infrared (FTIR) and ultraviolet–visible (UV–vis) spectra. The role of the initiator during vibromilling was also investigated.

## EXPERIMENTAL

### Materials

PVC (SG-8) with a number-average molecular weight of $5.0 \times 10^4$ was purchased from Jinlu Group, Ltd. (Sichuan, China). The r-LS, which contained both a piperidinyl structure and a conjugated bond, was obtained from the Institute of Chemical Industry (Shanxi, China; see Fig. 1). Both FTIR and UV–vis spectra of the r-LS are shown in Figure 2. Potassium persulfate ($K_2S_2O_8$) was obtained from Kelong Chemical Reagent Factory (Chengdu, China).

### Preparation of the polymeric photostabilizer

The photostabilizer was prepared through the mechanochemical reaction of PVC with the r-LS in a vibratory ball-milling machine developed in our laboratory.[16–20] PVC powder (200 g) and 20 g of the r-LS with various amounts of $K_2S_2O_8$ were added to the jar, which was loaded with steal balls. The reaction was conducted with various milling times, initiator contents, and temperatures at a rotational speed of 600 rpm with a 5-mm amplitude; the steel ball/mixture ratio was 10 : 1 (by mass), and the ball diameter was 14–18 mm. The temperature of the powder mixture during the process was controlled by a flow of cool water. The real-time temperature was monitored with a DM-6902 K-type thermometer (Victor Hi-tech Co., Shenzhen, China) during the pause time and immediately after the completion of the process.

### Purification

The milled mixture with a mass around 10.0000 g was extracted for 24 h by acetone in a Soxhlet extractor (Beijing Safelab Technology Ltd., Beijing,

China) to remove excessive r-LS and then was stored at 40°C in a vacuum oven for 24 h until a constant weight was obtained.

### Measurements and characterization

The infrared spectra of the samples were obtained with a Nicolet 560 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA). An approximately 1.0-mg sample with about 200 mg of dried KBr was ground in an agate bowl and then pressed into a transparent slice with a pressure of about 400 kg/cm$^2$ for about 2 min. Forty scans were acquired at a resolution of 1 cm$^{-1}$.

A U-3010 UV spectrophotometer (Hitachi Co., Ltd., Tokyo, Japan) in the wavelength range of 210–800 nm was used to obtain UV spectra of the samples, which were dissolved in tetrahydrofuran (THF), to investigate the development of double bonds. Gravimetric analysis[23] was used to calculate the amount of the r-LS grafted onto the PVC matrix with the following equation:

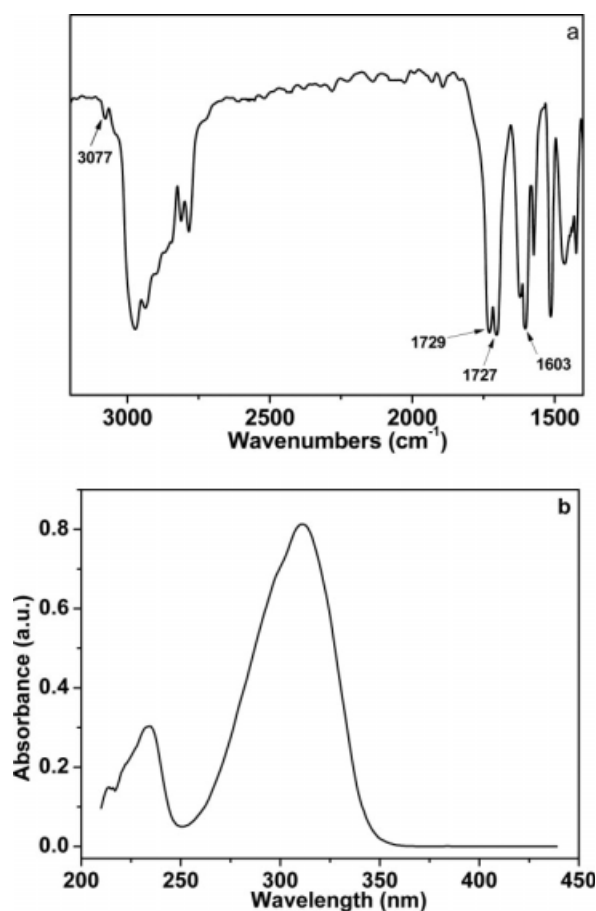$$G\% = \frac{(m_f + m_0) - m_t}{m_0} \times 100\%$$



**Figure 2** (a) FTIR and (b) UV–vis spectra of the r-LS (the concentration of the THF solution of the r-LS for UV–vis was 0.089 g/L).
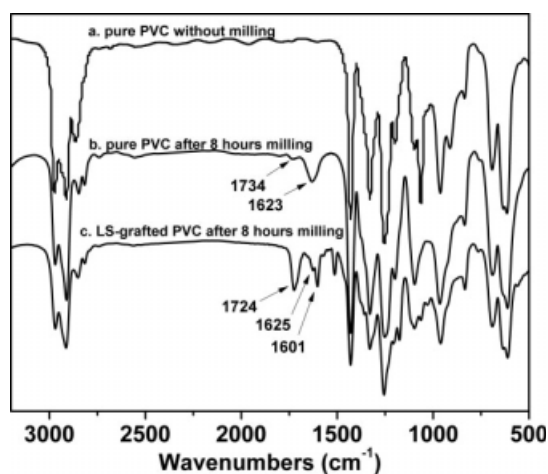
**Figure 3** FTIR spectra of (a) pure PVC without milling, (b) pure PVC after 8 h of milling, and (c) LS-grafted PVC after 8 h of milling.

where $m_0$ is the mass of PVC before milling, $m_t$ is the mass of the purified milled mixture, and $m_f$ is the mass of the filter paper.

Viscosity measurements were carried out with 1.0% solutions of LS-doped PVC in THF at 25°C with an Ubbelohde viscometer (Liangjing Co., Shanghai, China) that allowed dilution in the viscometer. For each sample solution, the flow time was measured at four different concentrations ($1C$, $2/3C$, $1/2C$, and $1/3C$). At least three readings were made at each of the four concentrations for each sample until variations in the flow time were kept within 0.2 s. On the basis of the four flow times, [η] of the sample was obtained. Then, according to the Mark–Houwink equation, [η] could directly reflect the change in the viscosity-average molecular weight.[5,9] [η] of PVC before milling was 1.2748 dL/g.

## RESULTS AND DISCUSSION

### Characterization of LS-grafted PVC

For comparison with LS-grafted PVC, the FTIR spectrum of pure PVC milled for 8 h is shown in Figure 3(a). The weak absorption of the carbonyl group at 1734 cm$^{-1}$ indicated that the oxidation reaction of PVC during this process could be ignored during vibromilling. This mechanochemical process mainly
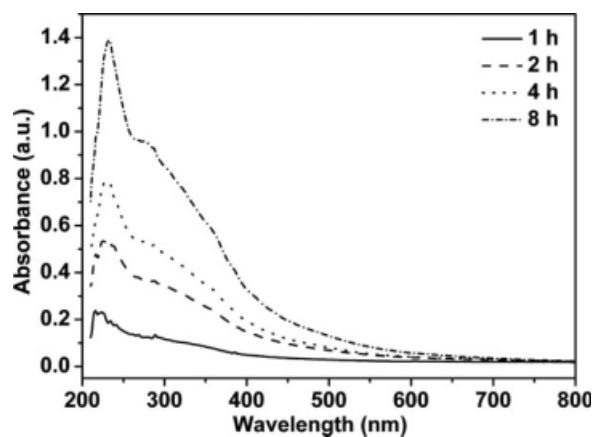


**Figure 4** Changes in the UV–vis spectra of pure PVC with the milling time.

induced the formation of vinyl groups (1623 cm$^{-1}$). The conjugated polyene sequences was verified by the UV–vis absorption profiles of pure PVC with the milling time, as shown in Figure 4. This gradual increase in the absorption intensity was attributed to the dehydrochlorination of PVC, which was similar to photodegradation or thermodegradation processes.[1,2,24]

Significantly different from the FTIR spectrum of pure PVC, the FTIR spectrum of LS-grafted PVC showed strong peaks at 1724 and 1601 cm$^{-1}$ after 8 h of milling [Fig. 3(c)]. Combining Figure 3(c) with the characteristic peaks of the r-LS at 1729 and 1603 cm$^{-1}$, we could conclude that the r-LS was grafted onto the PVC chains successfully.

### Effects of the vibromilling conditions on the grafting reaction

Initiator content

Table I presents the effects of the initiator content on $G\%$ and [η] of LS-grafted PVC. In comparison with the value in the presence of the initiator, the value without the initiator was low even after 8 h of milling. It was reasonable to conclude that the grafting reaction in the absence of the initiator was mainly triggered by the macroradicals produced by milling-induced main-chain scission of PVC. With the increase in the initiator content, $G\%$ increased

**TABLE I**
**Changes in $G\%$ and [η] with Various Initiator Contents**

| Code | Temperature (°C) | Time (h) | PVC | r-HALS | $K_2S_2O_8$ | $G\%$ | [η] (dL/g) |
|------|------------------|----------|-----|--------|-------------|-------|------------|
| I0 | 20 | 8 | 200 | 20 | 0 | 0.63 | 1.0027 |
| I1 | 20 | 8 | 200 | 20 | 0.5 | 4.29 | 0.9674 |
| I2 | 20 | 8 | 200 | 20 | 1 | 6.82 | 1.1812 |
| I3 | 20 | 8 | 200 | 20 | 2 | 7.35 | —[a] |

[a] The sample could not be completely dissolved in THF. r-LS, reactive light stabilizer.

**TABLE II**
**Changes in *G*% and [η] with Various Reaction Times**

| Code | Temperature (°C) | Time (h) | PVC | r-HALS | $K_2S_2O_8$ | *G*% | [η] (dL/g) |
|------|------------------|----------|-----|--------|-------------|------|------------|
| T0 | 20 | 0 | 200 | 20 | 0.5 | 0 | 1.2748 |
| T1 | 20 | 1 | 200 | 20 | 0.5 | 0.96 | 1.231 |
| T2 | 20 | 2 | 200 | 20 | 0.5 | 3.01 | 1.12 |
| T3 | 20 | 4 | 200 | 20 | 0.5 | 3.74 | 1.03 |
| T4 | 20 | 8 | 200 | 20 | 0.5 | 4.29 | 0.9674 |
| T5 | 20 | 12 | 200 | 20 | 0.5 | 4.48 | 1.2491 |
| T6 | 20 | 15 | 200 | 20 | 0.5 | 4.59 | —[a] |

[a] The sample could not be completely dissolved in THF. r-LS, reactive light stabilizer.

significantly, and this indicated that the addition of the initiator could facilitate the grafting reaction. As shown in Table I, a 0.5 phr concentration of the initiator made *G*% increase sharply. Unlike *G*%, the change in [η] was irregular with the addition of the initiator. In comparison with [η] of the sample without the initiator, [η] with the addition of 0.5 phr initiator slightly decreased. With the continuing increase in the initiator, [η] increased to 1.1812 dL/g from 0.9674 dL/g. Furthermore, the sample containing 2 phr initiator could not dissolve in THF because of the formation of the macrogels induced by the crosslinking reaction. On the basis of the results of *G*% and [η], it was clear that the initiator not only promoted the grafting reaction but also accelerated the crosslinking reaction of PVC. The mechanism of initiator-triggered reactions is elaborated in the Role of the Initiator in the Grafting Reaction section.

**Reaction time**

The data listed in Table II show the dependence of *G*% and [η] of LS-grafted PVC on the milling time of the mechanochemical reaction. *G*% was very low within 1 h and increased very quickly in the following hour. With the extension of the milling time, this increase tended to slow down slightly. After 15 h of milling, this value increased to 4.59%, but still no plateau appeared, and this showed that the grafting reaction did not finish completely. The very small *G*% value within 1 h might be attributed to the bad mixing of the PVC and r-LS at the beginning of the reaction. The marked increase in *G*% after 2 h of milling meant that the grafting reaction had occurred. The increase in *G*% with the milling time could be explained by the decomposition rate of the initiator, just like that of maleic anhydride grafted polypropylene.[22] The only difference was that after several hours, the grafting degree of maleic anhydride grafted polypropylene reached a plateau because of the completion of the grafting reaction, and the time was in agreement with the half-life of benzoyl peroxide. In our system, *G*% did not reach a plateau even after 15 h, and this indicated that the

reaction time was less than the half-life of our initiator.

[η] of LS-grafted PVC gradually decreased within 8 h, and this was in agreement with the results for pure PVC.[25–27] However, [η] jumped to 1.2491 dL/g after 12 h, and the sample could not be dissolved in THF after 15 h. It is well known that at a high shear stress, PVC chains can be seriously destroyed, and a lot of macroradicals will be produced.[25] At the same time, the initiator triggered more side-chain scission of PVC and initiated the primary radicals of the r-LS. Because of their short lifetime, these free radicals reacted rapidly with others, such as radicals on the polymer chains or introduced by the r-LS. On the basis of this complex interaction, on the one hand, the molecular weight of LS-grafted PVC decreased gradually; on the other hand, *G*% increased significantly. With the milling time extended to 12 h, the molecular weight of LS-grafted PVC began to increase, and after 15 h, the macrogels of LS-grafted PVC were formed. Therefore, we could conclude that more side-chain macroradicals were present after 12 h, and the recombination of the macroradicals of side-chain scission or the macroradicals of side-chain scission and macroradicals of main-chain scission induced the formation of macrogels of LS-grafted PVC.

**Reaction temperature**

The effects of the milling temperature on *G*% and [η] of LS-grafted PVC are shown in Table III. After 1 h of milling, *G*% at a high temperature (D1) was twice that at a low temperature (W1), whereas [η] of W1 was much greater than that of D1. After 8 h, *G*% at a high temperature (D2) was much smaller than that at a low temperature (W2). [η] of W2 decreased to 0.9674 dL/g, whereas that of D2 was not recorded because of the formation of macrogels that did not dissolve in THF completely. As known to all, the temperature controlled the decomposition rate of peroxide and accordingly influenced the concentration of the resulting free radicals. With the same milling time, the samples at a high temperature

| Code | Temperature (°C) | Time (h) | PVC | r-HALS | $K_2S_2O_8$ | $G\%$ | $[\eta]$ (dL/g) |
|------|------------------|----------|-----|--------|-------------|-------|----------------|
| D1 | 80 | 1 | 200 | 20 | 0.5 | 1.82 | 0.9814 |
| D2 | 80 | 8 | 200 | 20 | 0.5 | 3.81 | —[a] |
| W1 | 20 | 1 | 200 | 20 | 0.5 | 0.96 | 1.231 |
| W2 | 20 | 8 | 200 | 20 | 0.5 | 4.29 | 0.9674 |

[a] The sample could not be completely dissolved in THF. r-LS, reactive light stabilizer.

produced more free radicals, and these radicals not only accelerated the grafting reaction but also triggered the crosslinking reaction due to the formation of more side-chain macroradicals. On the basis of the results of $G\%$ and $[\eta]$, it was reasonable to assume that a high temperature facilitated both the grafting and crosslinking reactions simultaneously, but with the extension of the milling time (e.g., 8 h), the crosslinking reaction was accelerated, and this resulted in the formation of macrogels and a $G\%$ value lower than that of W2. Besides the influence of the temperature, the activation of the PVC, r-LS, and initiator resulting from high shear stress might play an important role in these reactions.

## Grafting reaction mechanism

As mentioned in the section on the characterization of pure PVC, a lot of conjugated polyene sequences were produced during milling, and this indicated that shear stress led to the degradation of PVC; the mechanochemical degradation mechanism has been extensively studied.[24,25] As shown in Figure 5, the imposition of excessive stress on the polymer chains caused the scission of chain bonds, which involved both main-chain scission and side-chain scission, after the appearance of a pair of macroradicals or a macroradical and a free chloride radical. Because of

the cage effect, the movement of these macroradicals was completely restricted, and this led to the predominance of a recombination reaction and disproportionation termination.[25] At the same time, chloride radicals produced during side-chain scission triggered the dehydrochlorination of PVC, and this resulted in the formation of a polyene sequence, as shown in Figure 4. During the milling process of pure PVC, the molecular weight decreased with the milling time, and no macrogels formed; it could be concluded from ref. 25 that main-chain scission predominated.

To further investigate the grafted products, UV–vis experiments were also carried out. As shown in Figure 6, the absorption intensity of the purified milled mixtures was different when the UV range was more than 350 nm. The intensity of UV absorption strongly depended on the milling conditions: At a high milling temperature (80°C), the absorption in a long UV range (>350 nm) was relatively strong, and this indicated that long conjugated polyene sequences were produced during this process.[1,2] At a low milling temperature (20°C), the absorption in this range was relatively weak, and this showed that a low milling temperature retarded the formation of conjugated polyene sequences and weakened the degradation of PVC. The extension of the milling time at the same temperature could also enhance the
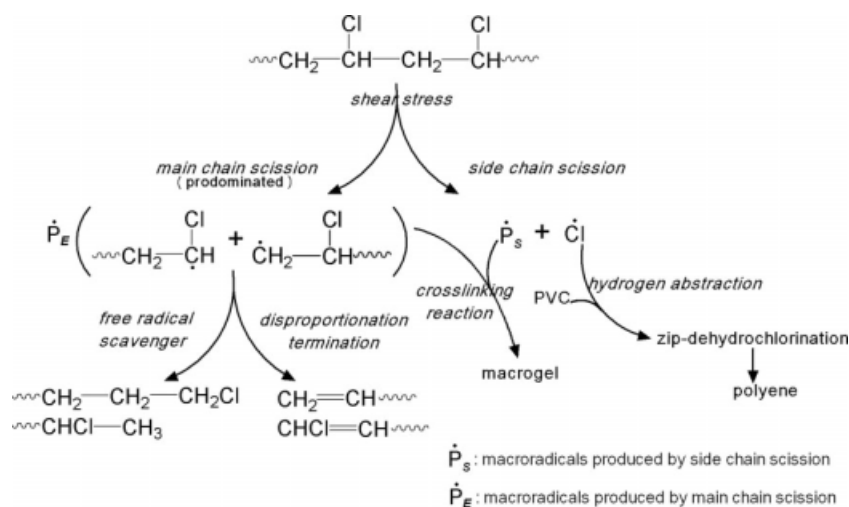


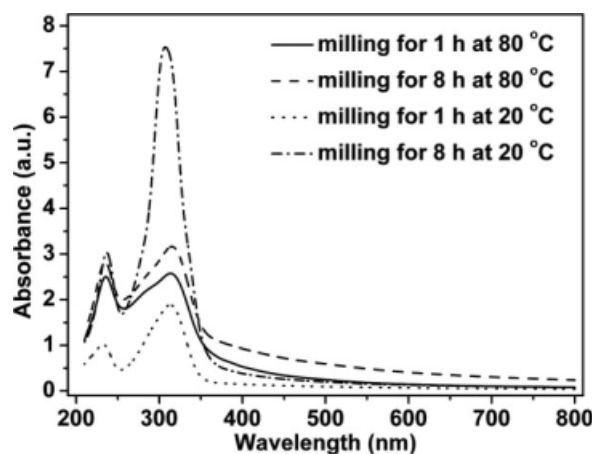**Figure 5** Mechanism of the mechanochemical reaction of pure PVC.

**Figure 6** UV–vis spectra of the purified milled mixture of the r-LS and PVC in the presence of the initiator.

absorption in this range (see the UV spectra in Fig. 4). All the absorption at wavelengths greater than 350 nm was triggered by the vibromilling-induced degradation of PVC, and the intensity of the absorption of the samples depended on both the milling time and reaction temperature, as discussed in the Effects of the Vibromilling Conditions on the Grafting Reaction section. In addition, the strong absorption peak at 300–330 nm, which was consistent with that of the r-LS, indicated that parts of the conjugated double bond of the r-LS still existed in the synthesized products after the grafting reactions, and the possible reactions are discussed in the Proposed Reactions section.

## Structure of LS-grafted PVC

In comparison with pure PVC, the resulting LS-grafted PVC revealed new absorptions at 1601, 1625, and 1724 cm$^{-1}$ in the FTIR spectra, and this
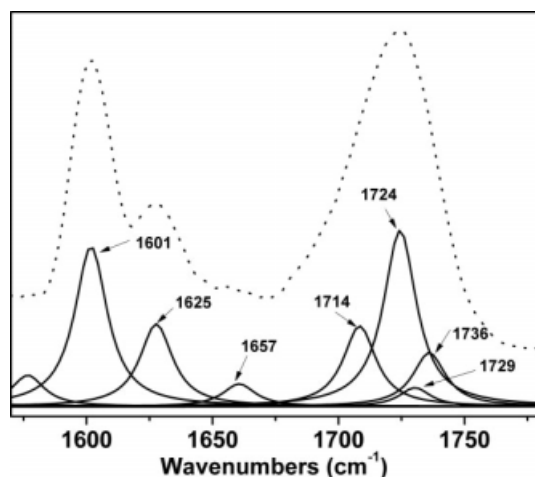


**Figure 7** Curve fitting of the FTIR spectrum of LS-grafted PVC in the presence of the initiator. The dotted line is the FTIR curve.
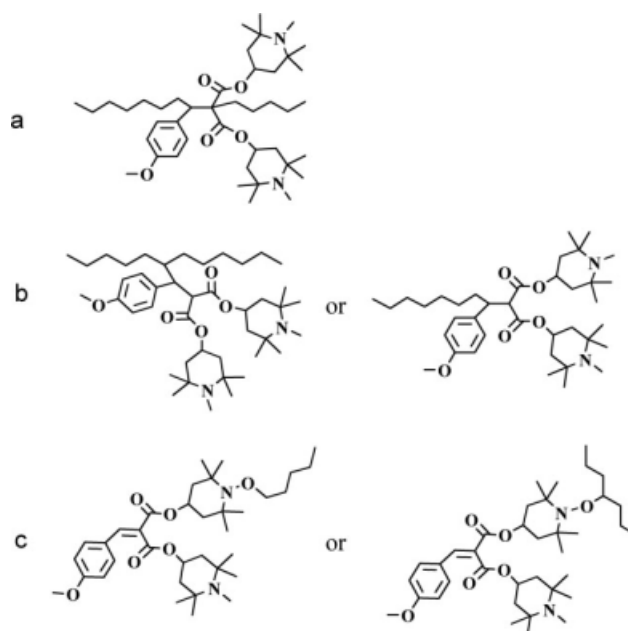


**Figure 8** Main structures of LS-grafted PVC: (a) the bridging type, (b) the end-grafting type (involving the side-grafting type), and (c) the N-O-PVC type.
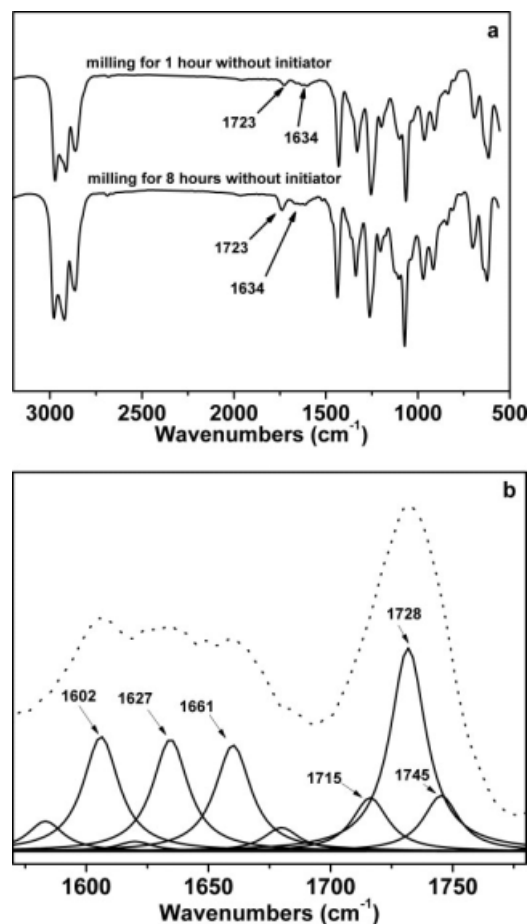




**Figure 9** (a) FTIR spectra of the milled mixture of the r-LS and PVC in the absence of the initiator and (b) curve fitting of the FTIR spectrum of LS-grafted PVC without the initiator. The dotted line is the FTIR curve.

indicated the successful grafting of the r-LS onto PVC chains. In our opinion, during the milling process, the conjugated double band of the r-LS participated in the free-radical addition reaction. At the same time, the results of the UV–vis spectra implied that parts of the conjugated structure of the r-LS still existed. The r-LS contained a piperidine structure, this structure was regarded as a free-radical scavenger, and it was important for preventing the UV irradiation of polymer materials. During the milling process, the piperidine structure might have scavenged the macroradicals produced by PVC and combined with the PVC chains.[28] It was reasonable to assume that the mechanisms of the grafting reactions involved both free-radical addition and free-radical scavenging processes. Because of the special structure of the r-LS (containing both a piperidine and a conjugated double band), in the presence of macroradicals, both of these reactions made the grafting of the r-LS onto the PVC chains successful. The absorption bands of LS-grafted PVC were mathematically analyzed by iterative curve fitting in the range of 1570–1780 cm$^{-1}$, and each absorption band was approximated by a Lorentzian function; the deconvoluted Lorentzians were considered the actual absorption bands, and the curve fitting of FTIR is shown in Figure 7. The absorption peaks at 1625 and 1736 cm$^{-1}$ corresponded to the vinyl and carbonyl groups that formed during the degradation of PVC,

respectively. The peaks at 1601 and 1657 cm$^{-1}$ were attributed to the C—H vibration of the phenyl group. The absorptions at 1714, 1724, and 1729 cm$^{-1}$ confirmed that there were three carbonyl groups, and this indicated that LS-grafted PVC was a mixture with main structures of a bridging type, an end-grafting type (involving a side-grafting type), and an N-O-PVC type which was produced during the combination of the piperidine structure of r-LS with the alkoxyl radical of PVC, as shown in Figure 8.

## Role of the initiator in the grafting reaction

The FTIR spectra of the purified milled mixture of the r-LS and PVC without the initiator, as shown in Figure 9(a), were similar to those of LS-grafted PVC in the presence of the initiator. The absorption bands for 8 h of milling were mathematically analyzed by iterative curve fitting in the range of 1550–1780 cm$^{-1}$, just as in Figure 7; the curve fitting of FTIR is shown in Figure 9(b). From the FTIR results for pure PVC, we knew that the oxidation reaction during the whole milling process was slight, and the peak of the carbonyl group was weaker than that of the conjugated double band, so the formation reaction of conjugated polyene sequences was predominated. After the addition of the r-LS, the new absorptions at 1728, 1715, and 1603 cm$^{-1}$ in the spectra were the characteristic peaks of LS-
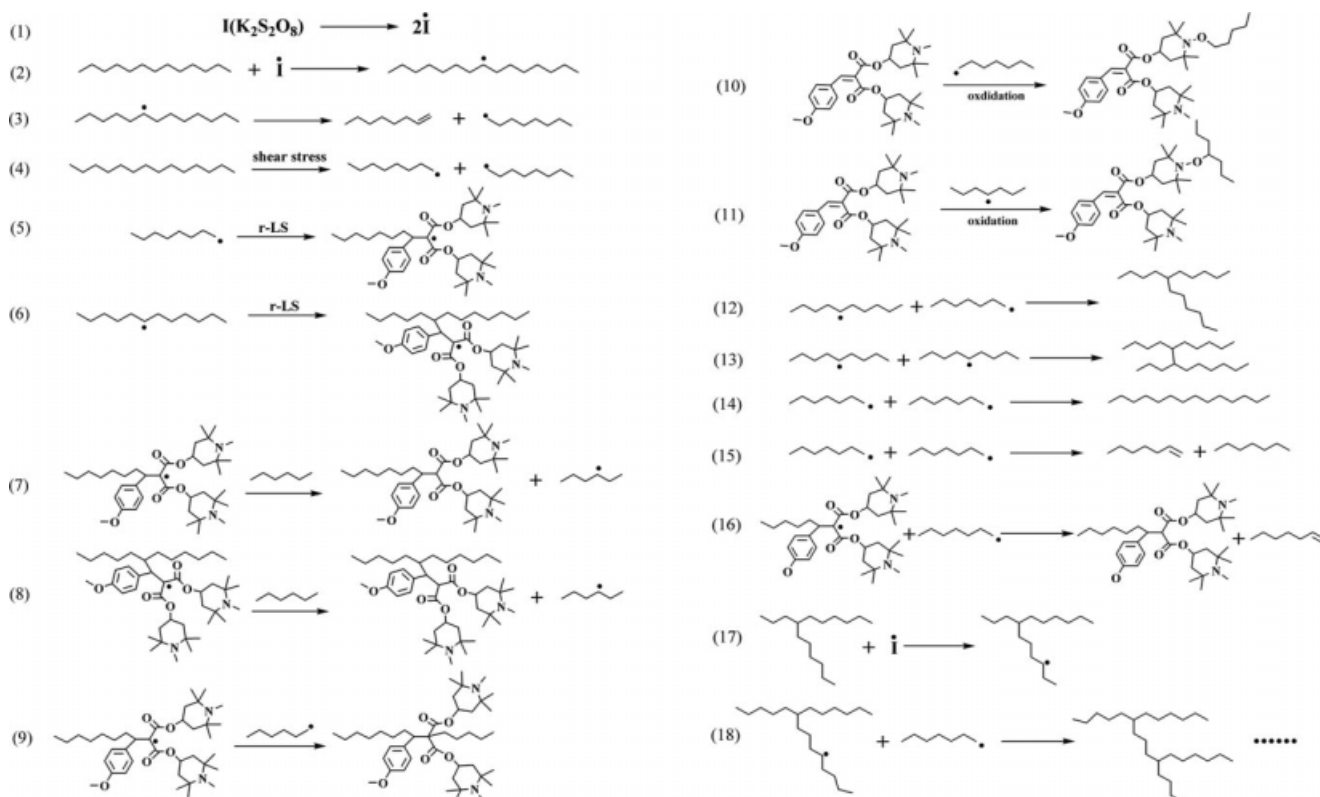


**Figure 10** Proposed reactions for the preparation of LS-grafted PVC by the vibromilling method.

grafted PVC. It could be concluded that vibromilling-induced macroradicals could also trigger the grafting reaction even without the initiator, although G% was very slight (Table III) and the corresponding FTIR peak was weak [Fig. 9(a)]. In fact, the grafting products in the absence of the initiator were also obtained for another system by a mechanochemical method.[21–22,29] The characteristic peak of LS-grafted PVC without the initiator was so weak that it could be concluded that the initiator played a very important role in the grafting reaction. It was reasonable to propose that because of the cage effect, macroradicals that formed during milling could not move freely, and this led to the increase in the probability of recombination and seriously retarded the grafting reactions. The initiator, just like the plasticizer, easily escaped from the PVC cage, continued to trigger both macroradicals and r-LS radicals, and thus significantly promoted the grafting reactions.

### Proposed reactions

On the basis of the aforementioned results and discussion, the main reactions are proposed in Figure 10.

First, the initiator decomposed to form primary radicals induced by vibromilling (reaction 1). The radical abstracted a hydrogen atom from the PVC chain and formed a side-chain macroradical (reaction 2). The side-chain macroradical underwent β scission to form an end macroradical chain end and a vinylidene chain end (reaction 3). However, in our opinion, this β-scission reaction was not serious because of the relatively low absorption of the carbonyl group. Just as shown in Figure 5, the imposition of excessive shear stress on the polymer chains caused the scission of chain bonds and played an important role in the decrease in the molecular weight (reaction 4).

Second, the r-LS was grafted onto both the side and end macroradical chains and formed the LS–PVC macroradicals (reactions 5 and 6). The LS–PVC macroradicals abstracted hydrogen from the PVC chains to form the PVC macroradicals and the LS–PVC molecules (reactions 7 and 8).

Finally, in the presence of radicals, the corresponding reactions competed with one another, and the termination reactions were complex and difficult to determine. The main possible reactions are proposed in reactions 9–14 for combination and in reactions 15 and 16 for disproportionation. Reactions 10 and 11 were responsible for the absorption at 250–350 nm in the UV–vis spectra.

In addition, factors such as the initiator content, temperature, and milling time induced the formation of macrogels, and the corresponding reactions are shown in reactions 17 and 18.

### CONCLUSIONS

A polymeric photostabilizer was prepared by the vibromilling grafting method, which was developed by Qiu and coworkers.[21,22] The r-LS was successfully grafted onto PVC chains, and the reaction mechanism was proposed. The optimum preparing conditions were 0.5 wt % initiator, 8 h of milling, and a low temperature. Under these conditions, a high G% value for PVC without macrogels could be obtained. On the basis of the results of FTIR and UV–vis spectra, the combination of radical addition and free-radical scavenging mechanisms could explain the grafting reactions successfully. The addition of the initiator effectively accelerated the grafting reaction because of the easy mobility and the capacity for the quick formation of macroradicals.

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