Crosslinking of Poly(Vinyl Chloride) with Bismaleic Compound. I. Crosslinking Mechanism

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SYNOPSIS

Crosslinked poly(vinyl chloride) (PVC) was obtained by using bismaleic compound (BMC). Styrene, as auxiliary crosslinker, can markedly promote the crosslinking course. After having carefully studied the gelling behavior of PVC in crosslinking, and the reactivity of styrene and BMC with PVC, the crosslink mechanism was suggested. The main crosslink reaction is the bridging of bismaleic compound between PVC macroradicals, which were created by thermal degradation of PVC and disproportionation of PVC with initiator radicals and styrene radicals. The first step of crosslink reaction was the BMC grafting on PVC macroradicals. Then styrene copolymerizes with active center bearing on bismaleic compound to propagate graft chain, which make bridging reaction easier to take place. At last, PVC* reacted with another double bond possessed by grafted BMC to form network structure

INTRODUCTION

Crosslinked PVC, due to the formation of network structure, has better heat and solvent resistance and more excellent mechanical properties.[1] Crosslinked PVC is used in many areas, such as wire coating, electrical insulator,[2] and airplane floor. We can obtain crosslinked PVC by radiation[3] or chemical agents.[4,5] The widely used chemical agents are azides,[6] dimercaptocompounds, diisocyanate/maleic anhydride/styrene,[7] divinyl compounds, and other polyfunctional monomers.[8]

As a divinyl monomer, bismaleic compound can crosslink poly(vinyl chloride) through grafting on PVC chains. It is generally believed that PVC chain attacked by radical at high temperature will create PVC macroradical (PVC*),[9] which can initialize divinyl monomer to copolymerize with it. At last, the crosslinked PVC will be obtained.
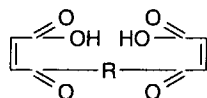
EXPERIMENTAL

Materials

All reagents and starting materials used in the course of this work were reagent grade and without any other purification. Bismaleic compound (BMC) was
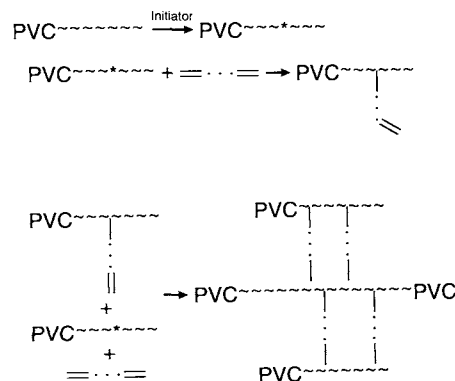
Scheme 1   Crosslinking of poly(vinyl chloride).

a specially synthesized compound with following structure:

Graft of Styrene on PVC

PVC containing 10% styrene (St), 4‰ dicumyl peroxide (DCP), and 80% dichloromethane was placed into a reactor and reacted for 20 min in oil bath at (160–190°C). The unreacted styrene and homopolymer of styrene was removed by THF and benzene.

Graft of BMC on PVC

A solution of 2 g PVC, 0.076 g BMC, 0.008 g DCP, and 1.6 g dichloromethane, which had been well mixed, was placed in a reactor. Let it react at a constant temperature (160–190°C). The unreacted BMC was removed by THF and methanol (Fig. 1).

Preparation of Crosslinked PVC

To a reactor were added 2 g PVC, 0.2 g St, 0.008 g DCP, 0.076 g BMC, and 1.6 g dichloromethane well-
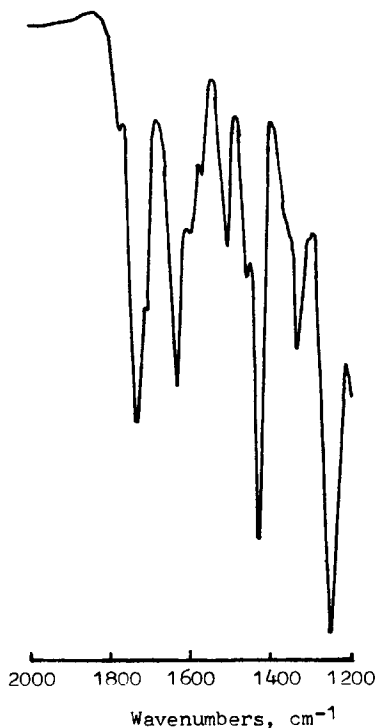

Figure 1   IR spectrum of PVC-BMC graft copolymer.

mixed. Place the reactor into oil bath with constant temperature (160–190°C). The crosslinked PVC would be obtained later.

Determination of Graft Efficiency

A solution of 1.00 g PVC grafted by BMC was solved by THF. The ungrafted BMC was insoluble in THF, which would be separated from solution by ultracentrifuge. From the weight of ungrafted BMC, we calculated the fraction of grafted BMC, i.e., graft efficiency (GE).

Determination of Gel-fraction Content

A solution of 1.00 g powdered crosslinked PVC, from which dichloromethane, unreacted monomers, and other volatile compounds had been removed, was abstracted by 50 mL THF for 48 h. The unsoluble PVC was separated from THF by ultra-centrifuge. From the weight of THF-unsoluble PVC, we calculated the gel-fraction content of crosslinked PVC.

RESULTS AND DISCUSSION

Crosslinking Reaction of PVC

Graft of Styrene on PVC

It is very difficult to study the crosslink reaction of PVC in the presence of styrene and BMC. So, we prefer to study the reaction of styrene with PVC at first. The experimental results show that styrene cannot be grafted onto PVC in our conditions (see Fig. 2). From the IR spectrum of reacted PVC from which the unreacted styrene and polystyrene had been removed, we do not find the phenyl absorption band (1495 and 695 cm^{-1}).

According to Doak's work,[10] the reactivity ratios of vinyl chloride (monomer 1) with styrene (monomer 2) are: $r_{12} = 0.02$, $r_{21} = 17$. The instantaneous mole fractions of copolymer can be expressed as follows:

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

$$= \left(1 + \frac{[M_2]}{[M_1]} \cdot \frac{r_{21}[M_2] + [M_1]}{r_{12}[M_1] + [M_2]}\right)^{-1}$$

$$F_2 = \frac{d[M_2]}{d[M_1] + d[M_2]}$$

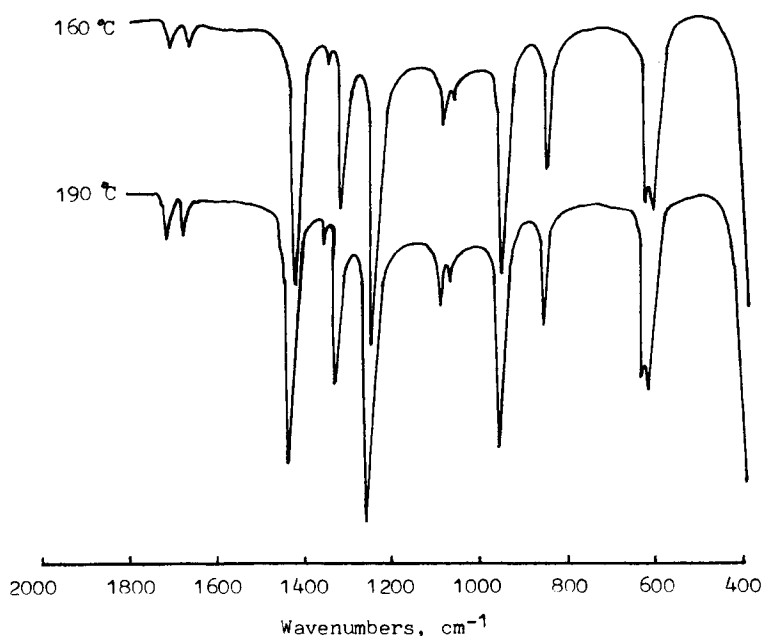$$= \left(1 + \frac{[M_1]}{[M_2]} \cdot \frac{r_{12}[M_1] + [M_2]}{r_{21}[M_2] + [M_1]}\right)^{-1}$$

Figure 2 IR spectrum of PVC having reacted with St for 20 min.

And M_1 includes all potential active center bearing on PVC, which can create PVC* if being attacked by radicals or acted by heat.

In our system, $[M_1]/[M_2] \rightarrow 0$; $r_{12}[M_1] \rightarrow 0$. Therefore,

$$F_1 \approx \frac{[M_1]}{2[M_1] + r_{21}[M_2]} \approx \frac{[M_1]}{17[M_2]} \rightarrow 0$$

$$F_2 = 1 - F_1 \rightarrow 1$$

This obviously indicates that styrene has strong tendency of homopolymerization. Styrene cannot be grafted to PVC chain in this situation. Of course, in other conditions, such as cationic copolymerization, styrene may be grafted to the PVC chain.[11]

Reaction of PVC with BMC

PVC containing BMC and DCP will crosslink at high temperature (see Table I). At lower temperature, graft reaction takes place only between PVC and BMC (see Table I).

Our experimental results show that BMC can be grafted onto PVC chain and form network structure at high temperature. The graft efficiency has a maximum value at about 180°C. But the gel-fraction is very small (about 5–6%).

Table I Graft Efficiency (GE) of BMC and Gel-fraction Content (GF) of PVC at Different Reaction Temperature

Reaction	Time (min)	8	10	12	14	16	18	20
160°C	GE (%)	8.2	11	14	22	30	36	41
	GF (%)	0	0	0	0	0	0	0
170°C	GE (%)	15	23	—	—	—	—	—
	GF (%)	0	0.4	1.2	2.9	4.3	5.6	7.0
180°C	GE (%)	26	—	—	—	—	—	—
	GF (%)	1.7	2.8	4.0	5.8	6.9	8.0	8.9
190°C	GE (%)	14	—	—	—	—	—	—
	GF (%)	0.5	1.4	3.0	4.5	5.2	5.6	5.8

$$PVC \xrightarrow[\Delta]{DCP} PVC^*$$
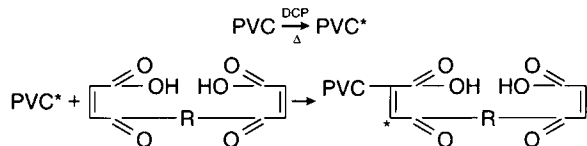
Scheme 2 Produce of PVC–BMC graft copolymer.

According to our former work, the reactivity ratios of VC (monomer 1) with BMC (monomer 3) are $r_{13} = 0.42$, $r_{31} = 0$.

$$F_1 = \left(1 + \frac{[M_3]}{[M_1]} \cdot \frac{r_{31}[M_3] + [M_1]}{r_{13}[M_1] + [M_3]}\right)^{-1}$$

$$= \frac{[M_3] + 0.42[M_1]}{2[M_3] + 0.42[M_1]}$$

In our system, $[M_1]/[M_3] \rightarrow 0$. Therefore, $F_1 \rightarrow 0.5$; $F_3 \rightarrow 0.5$.

It indicates that BMC tends to copolymerize with PVC chain, and PVC* tends to copolymerize with BMC. Therefore, BMC can be easily grafted onto the PVC chain.

When reaching definite graft efficiency, another unreacted double bond bearing on grafted BMC will react with other PVC* to form crosslinked PVC.

Because of strong space hindrance, the probability of these reactions taking place is very small. Therefore, we cannot obtain high gel-fraction content, if only depending on bismaleic compound.
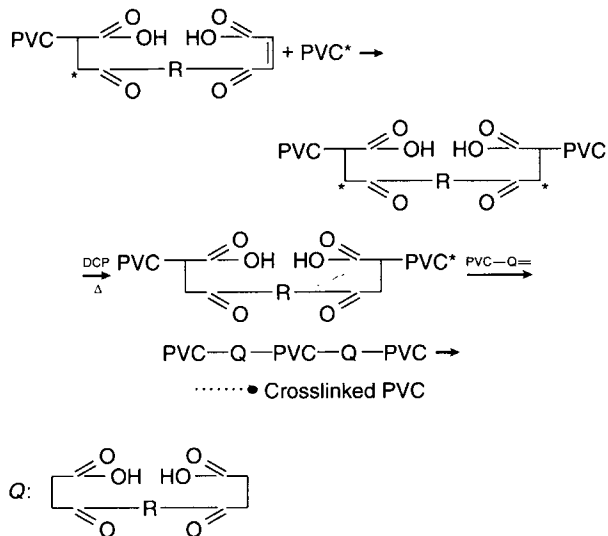
Scheme 3 Produce of crosslinked PVC.
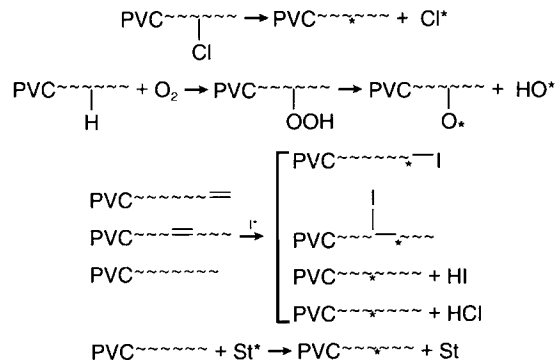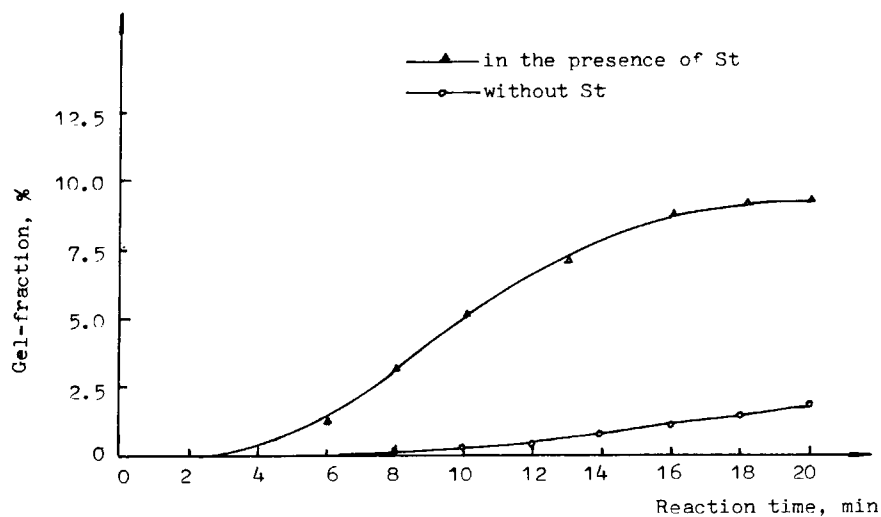

Scheme 4 Crosslinking course.

Figure 3 Effects of St on gelling speed of PVC at 170°C, 6 phr BMC.
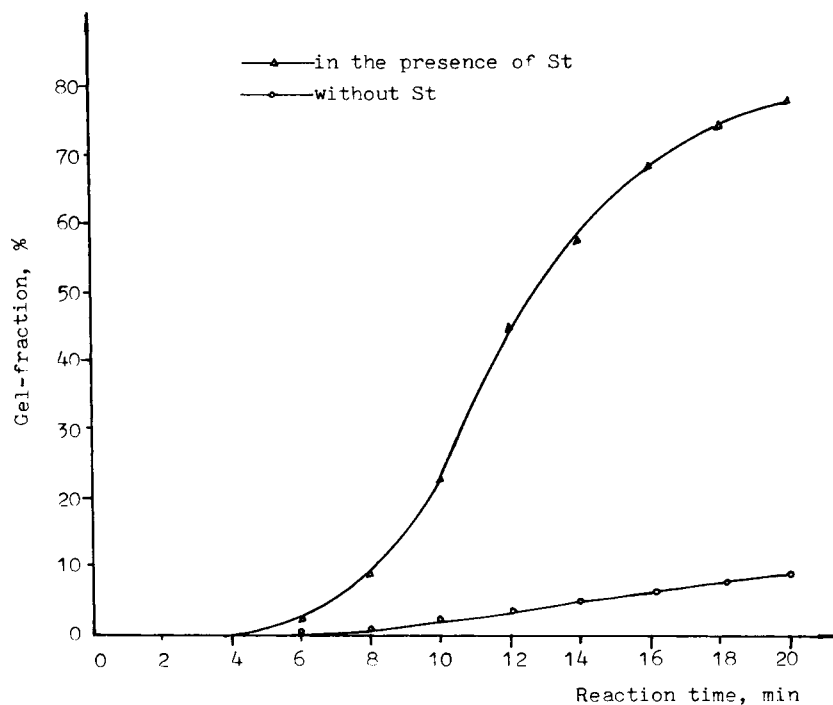
Figure 4   Effects of St on gelling speed of PVC at 180°C, 6 phr BMC.

Reaction among PVC, St, and BMC

As shown in Figs. 3, 4, and 5, St markedly accelerates the crosslinking course of PVC. Thus St tends to produce AB-type copolymer with BMC, which enlongs the graft chain and increases the reactivity of uninitialized double bond bearing on grafted BMC.

Crosslinking Mechanism

Creation of PVC Macroradicals (PVC*)

As reported by Gillen et al.,[12-15] PVC will degrade to produce PVC* at high temperature or when attacked by monomer radicals.
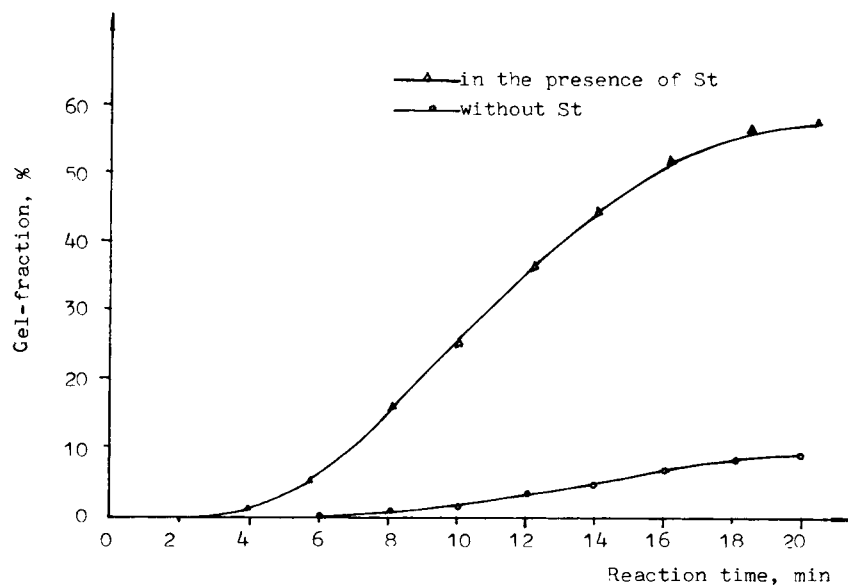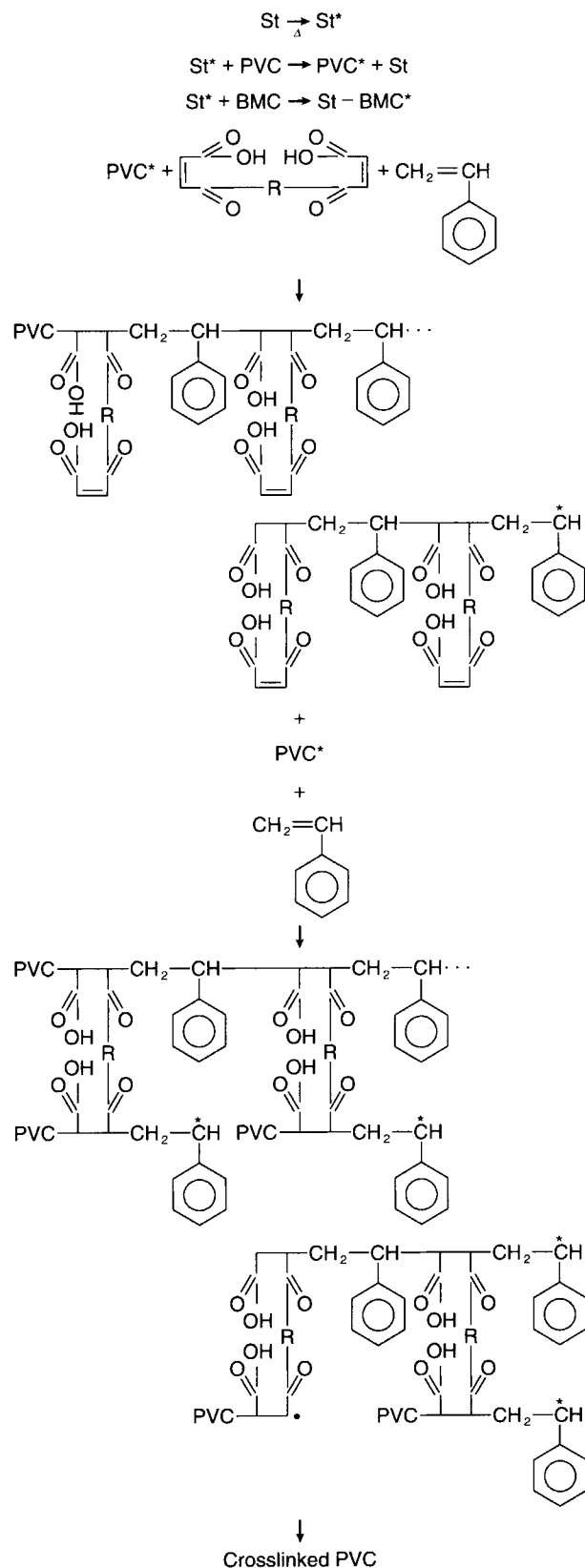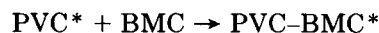

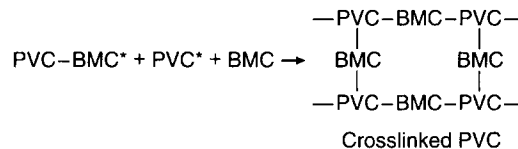**Figure 5**   Effects of St on gelling speed of PVC at 190°C, 6 phr BMC.

Scheme 5   Crosslinking of PVC.

In the absence of St, PVC* tends to react with BMC to produce PVC–BMC*, as indicated earlier.

$$PVC^* + BMC \rightarrow PVC\text{–}BMC^*$$

PVC–BMC* will further react with PVC* to form crosslinked PVC.

$$PVC\text{–}BMC^* + PVC^* + BMC \rightarrow \begin{array}{c} -PVC\text{–}BMC\text{–}PVC- \\ | \qquad\qquad | \\ BMC \qquad BMC \\ | \qquad\qquad | \\ -PVC\text{–}BMC\text{–}PVC- \end{array}$$

Crosslinked PVC

In the presence of St, our experiments indicated that St (monomer 2) tends to copolymerize with BMC (monomer 3) to produce AB-type copolymers ($r_{23} = 0.02$, $r_{32} = 0$).

Acted on by heat, St produces St* by itself. St* will attack BMC and PVC to create BMC* and PVC*.

As we expected, St can promote the crosslinking course of PVC, because St can act as an auxiliary crosslinker. In addition, St itself can produce radicals that help the forming of PVC macroradicals.

CONCLUSION

Bismaleic compound as crosslinker of PVC is very effective and practical. The crosslinking mechanism is the bridging of bismaleic compound between PVC macroradicals created by thermal degradation of PVC itself and disproportionation of PVC with initiator radicals and styrene radicals. Styrene as auxiliary crosslinker can obviously promote grafting of BMC on PVC chain, and accelerate the crosslinking course.

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