

Copolymerization of Styrene-*m*-Divinylbenzene in the Presence of Poly(vinyl Chloride)

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Synopsis

The crosslinking copolymerization of styrene (St)-*m*-divinylbenzene (*m*-DVB) in the presence of poly(vinyl chloride) (PVC) was studied. The rate of the copolymerization decreased with the addition of PVC powder, because of the depressing of the diffusion of the monomers to the polymerizing center and the difficulty in the transfer of the polymer radicals in the swelled PVC powder. The exponential value of the benzoyl peroxide concentration and the activation energy of the copolymerization were obtained as 0.67 and 17.4 kcal/mol, respectively. The monomer reactivity ratios of St and *m*-DVB were determined as $r_1 = 0.25$ and $r_2 = 1.42$ (M_1 : St, M_2 : *m*-DVB). From the extraction of the resultant polymer composite with THF, both the grafting of the St-*m*-DVB copolymer onto PVC and the entanglement of PVC with St-*m*-DVB copolymer seems to occur in the St-*m*-DVB-PVC system.

INTRODUCTION

The copolymerization of vinyl monomer-divinyl monomer has widely been studied, and it is known that the copolymerization is considerably affected by the presence of divinyl monomers.¹⁻⁶ However, the details of the copolymerization have not fully been elucidated yet because the characterization of the crosslinked copolymer is difficult. Wiley et al.^{7,8} and Malinsky et al.⁹ have studied the copolymerization of styrene (St)-divinylbenzene (DVB) by tracer and IR technique and have discussed the monomer reactivity ratios.

We have been interested in the crosslinking copolymerization and one of us,^{10,11} studied the precipitating copolymerization: copolymerizations of glycidyl methacrylate-DVB in cyclohexane¹⁰ and monoalkyl maleate-maleic anhydride-St-DVB in benzene.¹¹ In these cases, the resultant copolymer precipitates out of the copolymerization medium to yield a fine, powdery polymer because of its insolubility. Also, the crosslinking copolymerization in the presence of a polymer soluble in the monomers is very interesting, and the copolymerization of St-DVB in the presence of Hypalon (an elastomer) was studied to clarify the effect of the elastomer.¹² Then, the crosslinking copolymerization in a polymer gel phase was considered to be interesting, so we investigated the copolymerization of St-*m*-DVB in the presence of polyvinyl chloride (PVC) powder which was not soluble but swellable in the monomers at the copolymerization conditions.

EXPERIMENTAL

Materials

The purification of styrene (St), *m*-divinylbenzene (*m*-DVB), and benzoyl peroxide (BPO) was described in a previous paper.¹² Poly(vinyl chloride) (PVC) powder of commercial grade was washed with a methanol-water mixture and dried at 60°C under vacuum. The particle diameter of the PVC was 0.3–0.7 μm . Dioctyl phthalate (DOP) was of commercial grade. DOP was used in order to adjust the viscosity of the paste, because DOP is widely used in the processing of PVC.

Copolymerization

The standard recipe for the copolymerization (St/*m*-DVB/PVC/DOP/BPO = 9/1/3/0.3/0.1 by weight) was used in this study unless noted otherwise. PVC was added to the monomer mixture and well mixed. The resultant paste, of viscosity 0.4 poise at 25°C, was then put into an ampoule (70 mm in length and 12 mm in diameter) under nitrogen atmosphere in the dark. The copolymerization was initiated by immersing the ampoule in an oil bath maintained at a definite temperature. After a definite time, the copolymerization was stopped by immersing the ampoule in a Dry Ice-methanol bath. The resultant polymer composite was put into tetrahydrofuran (THF) containing 0.5% *p*-benzoquinone, and the mixture was subsequently poured into excess methanol. The precipitated copolymer was filtered by means of a 4G glass filter, washed with methanol, and dried at 60°C under vacuum for 16 hr.

Determination of the Copolymer Composition

The conversion was determined by subtracting the amount of PVC in the copolymerizing system from that of the resultant polymer composite. When PVC was present in the system, the resultant polymer composite was obtained as a fine powder after putting the copolymer mixture into THF, so the unreacted monomers were completely excluded from the resultant crosslinked polymer composite. The residual monomers were analyzed with the aid of gas chromatography by using butylcellosolve as the internal reference in the THF solution (column PEG-36000, carrier gas hydrogen, and temperature 105°C). The copolymer composition was determined by IR spectrometry.

The fine powdery polymer composite was used as the sample for KBr-method IR spectrometry, and the following characteristic bands were used: 795 cm^{-1} (out-of-plane deformation vibrations of the *m*-substituted aromatic ring in poly(*m*-divinylbenzene) and 760 cm^{-1} (out-of-plane deformation vibrations of monosubstituted aromatic ring in polystyrene). Figure 1 shows the relation between the conversions determined by gas-chromatographic and gravimetric methods. Both conversions in the range of 30%–70% were consistent; therefore these copolymers were used as the standard samples for the IR spectrometry. The calibration curve is shown in Figure 2. Copolymer composition was determined by using this curve. The PVC content of the copolymer was calculated from the chlorine content of the copolymer determined by the elementary analysis.

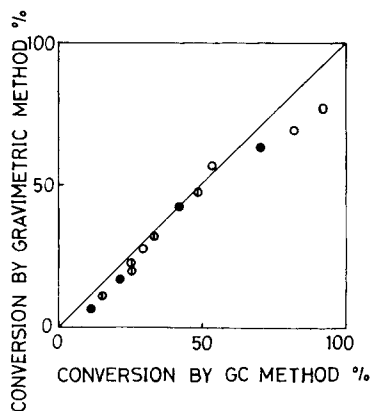


Fig. 1. Relationship between conversions obtained by gravimetric and gas-chromatographic methods. Copolymerization conditions: PVC/St-*m*-DVB = 1/3, BPO 0.1 phm, 70°C: (○) *m*-DVB/St = 0.25; (●) *m*-DVB/St = 1; (⊖) *m*-DVB/St = 4.

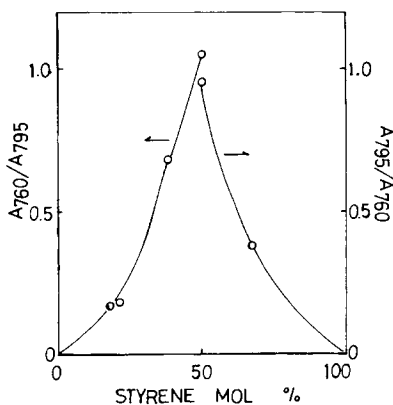


Fig. 2. Calibration curve of IR analysis.

Extraction with Tetrahydrofuran

The sample was extracted with THF for 24 hr under nitrogen atmosphere with of a Soxhlet apparatus, and the following symbols were assigned to the separated fractions (see Table I):

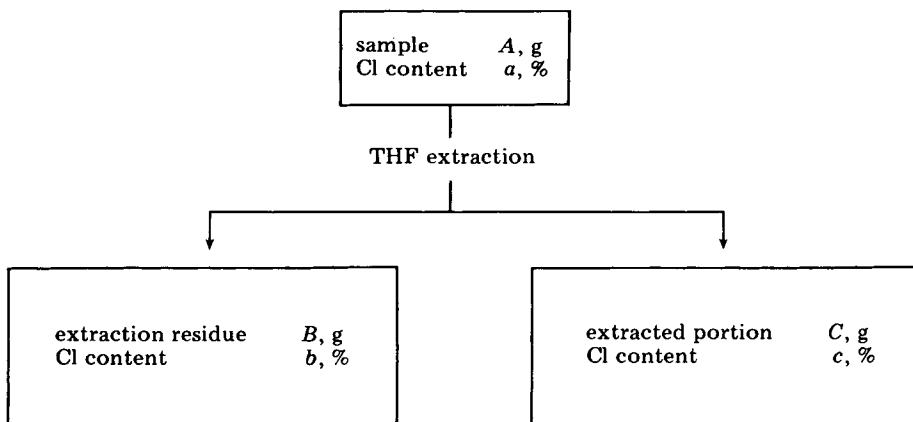


TABLE I
THF Extraction

No.	Monomer ratio in recipe by weight St- <i>m</i> -DVB/ PVC	St- <i>m</i> -DVB copolymer		Extracted portion							
		Con- ver- sion, ^a %	content in sample, ^b wt. %	Extraction residue			St- <i>m</i> -DVB copolymer content,				
				B/A	<i>b</i> , %	PVC content wt. %	C/A	<i>c</i> , %	wt. %	<i>Ep</i>	<i>Er</i>
1	4/1/5	96.1	49.0	0.778	21.43	37.8	0.192	53.02	6.4	0.624	0.025
2	2.5/2.5/5	87.0	46.5	0.801	26.22	46.3	0.180	54.89	3.1	0.685	0.013
3	1/4/5	69.0	40.8	0.794	26.00	45.9	0.188	55.22	2.6	0.665	0.011

^a Copolymerized at 80°C.^b Calculated from Cl content.

The cylindrical filter paper used was Toyo filter paper No. 84 (size 25 mm × 90 mm); the particle size retainable by this filter paper is 8 μm. The extracted portion (*Ep*) and the extraction residue (*Er*) were defined as follows:

$$E_p = \frac{\text{Cl content of the extraction residue (} b \text{)}}{\text{Cl content of the sample (} a \text{)}}$$

$$E = \frac{\text{quantity of St-}m\text{-DVB copolymer in the extracted portion}}{\text{quantity of St-}m\text{-DVB copolymer in the sample}}$$

RESULTS AND DISCUSSION

When PVC was not used, the resultant St-*m*-DVB copolymer at the low conversions was dissolved or allowed to swell in THF. Consequently, the unreacted monomers can be completely separated from the copolymer, so that the precise conversion could be determined. However, at higher conversions the precise conversion could not be determined because the copolymer did not swell enough in THF. On the other hand, when PVC powder was used, the resultant polymer composite swelled in THF even at higher conversions and became a fine powder when the THF mixture was placed into excess methanol, so that the correct conversion could be determined.

Figure 3 shows the effect of PVC on the polymerization of St and the copolymerization of St-*m*-DVB. The rates of polymerization and copolymerization in the presence of PVC were smaller than those in the absence of PVC. When a polymer was dissolved in the system, the copolymerization rate of St-*m*-DVB increased by the addition of the polymer, as reported in the case of the St-DVB-Hypalon system.¹² These results may be explained as follows. When the polymer was soluble in the system, the increase in the viscosity of the system resulted in autoacceleration of the copolymerization. However, in the presence of PVC, PVC was not dissolved in the St-*m*-DVB system but only swelled at the polymerization temperature although the apparent viscosity of the solution increased. Therefore, the diffusion of the monomers and the polymer radicals in the swelled PVC powder became slower and the rate of the copolymerization was depressed.

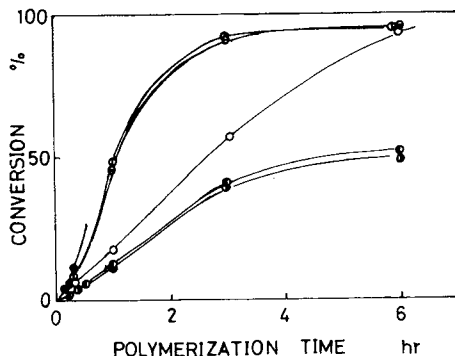


Fig. 3. Effect of PVC on copolymerization of St-*m*-DVB. Copolymerization conditions: BPO 1 phm, 80°C. St/*m*-DVB/PVC (weight ratio): (○) 1/0/0; (◐) 2/0/1; (●) 10/1/10; (◑) 10/1/4; (◒) 10/1/6; (◓) 3/0/1.

A plot of the initial polymerization rate (R_p) versus BPO concentration shows a linear relationship (Fig. 4). R_p was determined at a conversions of less than 10% by the Bamford-Jenkin's method.¹³ The exponential value of the BPO concentration, obtained from the slope of the straight line in Figure 4, was 0.67 and larger than 0.5. This result means that monomolecular and bimolecular terminations occur simultaneously in the system. This phenomenon may be due to the limited mobilities of the propagating radicals because of the relatively high viscosity of the system. For reference, the exponential value of the BPO concentration in the St-*m*-DVB-Hypalon system was 0.61.¹²

The effect of *m*-DVB at rather low concentrations on the copolymerization rate is shown in Figure 5. The copolymerizations rate considerably increased with increase in the *m*-DVB quantity even in the presence of PVC, as reported in the literature.¹⁻³ At higher concentrations of *m*-DVB, the copolymerization rate also increased with increase in the *m*-DVB quantity at the initial stage of the copolymerization, but the tendency was reversed at high conversions (Fig. 6). This phenomenon may be explained as follows. At the initial stage, the copolymerization rate increased with increase in the *m*-DVB quantity owing to the autoaccelerating effect of *m*-DVB; but in the case of the rather high concentration of *m*-DVB, the crosslinking density became fairly high and the diffusion of the monomers to the active radical became slower.

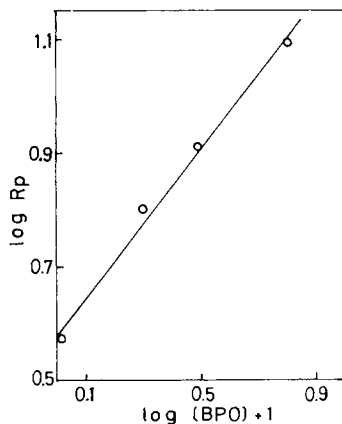


Fig. 4. Plot of R_p vs BPO concentration.

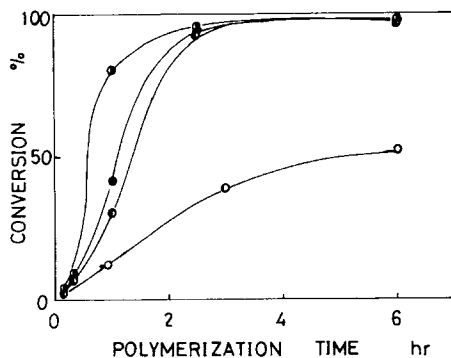


Fig. 5. Effect of *m*-DVB on copolymerization at 80°C. *m*-DVB/*St*-*m*-DVB: (○) 0, (●) 0.035; (●) 0.072; (●) 0.107.

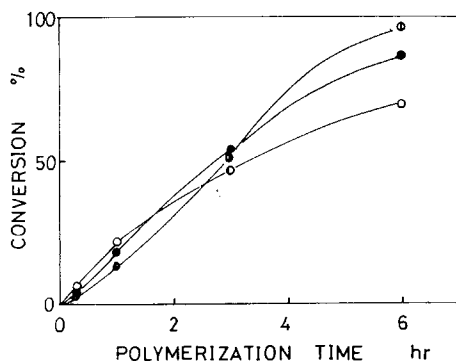


Fig. 6. Effect of *m*-DVB on copolymerization at the higher concentration at 70°C. *m*-DVB/*St*-*m*-DVB: (⊙) 0.45p (●) 0.54; (○) 0.80.

The effect of temperature on the copolymerization rate is shown in Figure 7. Figure 8 shows the Arrhenius plot. The activation energy was calculated to be 17.4 kcal/mol from the slope of the straight line in Figure 8. The activation energies for the copolymerization of *St*-*m*-DVB were as follows: 20 kcal/mol in the bulk,¹⁴ 15 kcal/mole in *t*-butylbenzene,¹⁵ and 21 kcal/mol in the presence of Hypalon.¹²

A small amount of *t*-butylcatechol, a radical scavenger, did not affect the

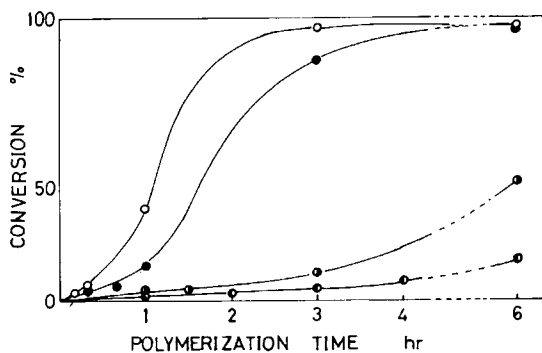


Fig. 7. Effect of temperature on the copolymerization: (○) 80°C; (●) 70°C; (●) 60°C; (●) 53°C.

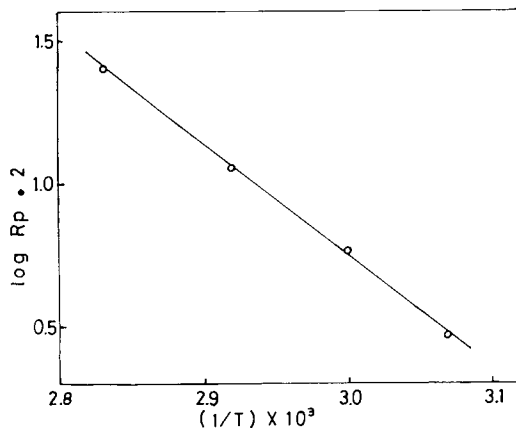


Fig. 8. Arrhenius plot.

shapes of the time-conversion curves of the copolymerization, but delayed the initiation (Fig. 9). However, when more than 0.2% *t*-butylcatechol was used, the copolymerization rate decreased, because the corresponding amount of BPO was consumed by *t*-butylcatechol before the onset of the copolymerization.

The monomer reactivity ratios of St and *m*-DVB were determined by the usual method. Copolymerization at a conversion of less than 5% is necessary to obtain good results. However, the resultant polymer composite at a conversion of less than 5% contained too much PVC; the precise determination of the composition was difficult because the absorption bands of 760 and 795 cm^{-1} were disturbed by the absorption band of PVC (600–700 cm^{-1}). The resultant polymer composite was therefore carefully washed with a methanol-THF (2/3) mixture which dissolved PVC but not St-*m*-DVB copolymer.

The Finemann-Ross plot is shown in Figure 10, showing a good linear relation. The plot was not affected by the presence of PVC, and consequently the monomer reactivity ratios in the system were the same as those in the absence of PVC. The values of r_1 (St) and r_2 (*m*-DVB) were 0.25 and 1.42, respectively. These values are a little different from the values of $r_1 = 0.34$ and $r_2 = 1.20$ by Wiley.⁷ *m*-Divinylbenzene contains two double bonds in the molecule, so when the concentration of the vinyl group of *m*-DVB is calculated as twice the molar concentration of *m*-DVB, values of $r_1 = 0.35$ and $r_2 = 80.96$ are obtained. The

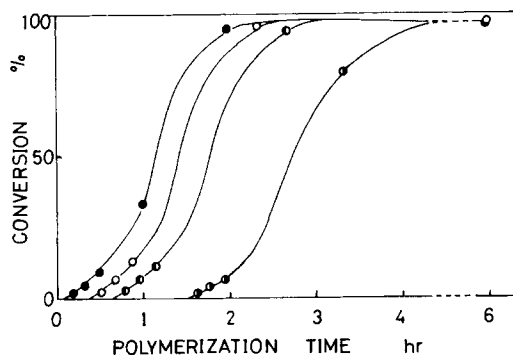


Fig. 9. Effect of *t*-butylcatechol (in %/monomers) on copolymerization. *t*-butylcatechol concentration: (●) 0.20; (◐) 0.07; (○) 0.03; (●) 0.

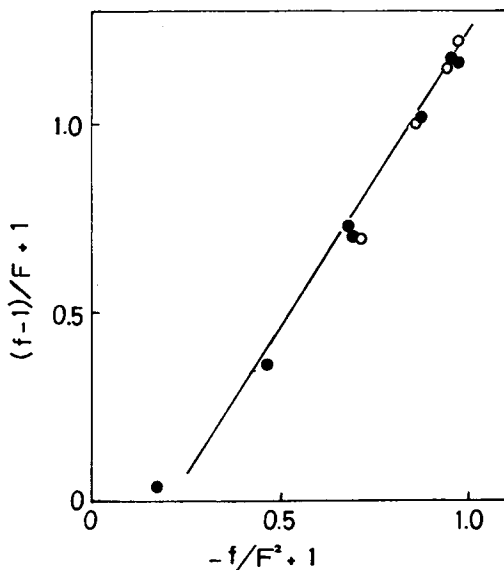


Fig. 10. Fineman-Ross plot: f ; molar ratio of St/*m*-DVB in copolymer; F ; initial molar ratio of St/*m*-DVB; (●) PVC/St-*m*-DVB = 1/2; (○) PVC/St-*m*-DVB = 0.

corresponding values reported by other investigators are: r_1 and r_2 , 0.605 and 0.88¹⁶; 0.77 and 1.08¹⁶; 1.11 and 1.00¹⁷; 0.54 and 0.58⁹; and 0.60 and 0.65.⁸ The copolymer composition at all the conversions was calculated by using values of $r_1 = 0.25$ and $r_2 = 1.42$ by means of a computer according to Brown's¹⁸ and Montgomery's methods.¹⁹ The relation between the observed and calculated values is shown in Figure 11. When the *m*-DVB content in the recipe was relatively large, the two values were in good agreement with each other. But when the *m*-DVB content was relatively small, the two values tended to differ a little. The result may be ascribed to measurement error of the absorption band at 795 cm^{-1} in the IR spectrum, because the absorption band is weak when a small amount of *m*-DVB is used.

To elucidate the interrelation of PVC with the St-*m*-DVB copolymer, the resultant polymer composite was extracted with THF under nitrogen atmosphere

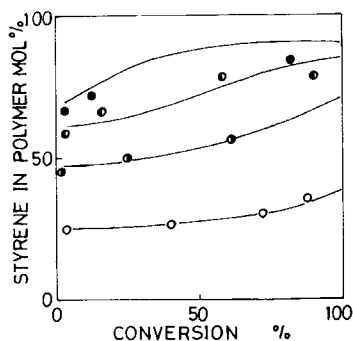


Fig. 11. Copolymer composition curves calculated by using $r_1 = 0.25$, $r_2 = 1.42$, and values obtained experimentally (at 80°C). St/*m*-DVB (weight ratio): (○) 48/62; (◐) 71/29; (◑) 85/15; (●) 90/10.

for 24 hr. The results are shown in Table I. The recovery ratio was more than 98%. Considering the fact that PVC is easily soluble in THF and that the St-*m*-DVB copolymer is insoluble, it is remarkable that the St-*m*-DVB copolymer can be found in the extracted portion, albeit in small amounts, and that a fair amount of PVC (about 20%) remains in the extraction residue. This shows that some interaction takes place between the St-*m*-DVB copolymer and PVC: grafting of St-*m*-DVB onto PVC and entanglement of PVC with the three-dimensional matrix of the St-2*m*-DVB copolymer. Furthermore, the *Ep* value shows that more than half (62.4%–66.5%) of PVC in the recipe remains in the extraction residue, and the *Er* value shows that almost none of the St-*m*-DVB copolymer is extracted. However, it is noteworthy that a small amount of the copolymer is extracted via the filter paper.

As reported so far, polystyrene is incompatible with PVC, so that during the copolymerization process the resultant St-*m*-DVB copolymer is separated out of the PVC phase and *m*-DVB promotes the phase separation. As a result, the St-*m*-DVB copolymer of colloidal dimension is dispersed in the PVC phase.²⁰⁻²² Furthermore, the polymerization of St in a PVC film results in grafting of St onto PVC.²³ Accordingly, both the grafting of the St-*m*-DVB copolymer onto PVC and the entanglement of PVC with the St-*m*-DVB copolymer is surely concerned with the results described above, although to what degree is still uncertain. Thus, the presence of PVC in the extraction residue can be explained.

On the other hand, the presence of the St-*m*-DVB copolymer in the extracted portion can be explained as follows: Considering the use of *m*-DVB, the propagating copolymer radical cannot migrate in the PVC gel phase, and the diffusion of the monomers to the active radical must be considerably restricted, owing to the three-dimensional matrix of the St-*m*-DVB copolymer and the PVC gel phase. The resultant St-*m*-DVB copolymer is thus very minute and can partially pass through the filter paper, as supported by previous studies.²⁰⁻²² Here, it is not confirmed whether the soluble polymer was present in the extracted portion.

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