Preparation and Characterization of Polystyrene Terminated with an Organic Sulfide Group and Styrene–Vinyl Acetate Block Copolymer

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SYNOPSIS

Polystyrene terminated with an organic sulfide group was prepared by styrene bulk polymerization using three organic disulfides as initiators, and the content of the organic sulfide group ($\bar{X}_n$) was determined quantitatively from the data of UV and $\bar{M}_n$.

Styrene–vinyl acetate block copolymer was prepared by using polystyrene ended with the organic sulfide group as the photosensitizer to initiate vinyl acetate polymerization. The copolymer was characterized by IR, ^{1}H-NMR, ^{13}C-NMR, DSC, and TEM, respectively.

Different copolymerization conditions were investigated systematically. The result reveals that the $\bar{X}_n$ value is a key factor in the copolymerization and the copolymerization proceeds via living radical mechanism. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Styrene–vinyl acetate block copolymer chain contains two kinds of pendant groups, one of which (acetate group) can be hydrolyzed into hydroxyl, the other (phenyl group) can be further functionalized. Because of the reactivity ratio[1-2] of styrene and vinyl acetate, however, the copolymerization of styrene with vinyl acetate is virtually impossible when classical methods of polymerization are used.

In certain cases, copolymerization was achieved by using macromer,[3] macroradicals,[4-5] or polymer with a functional group that can produce polymer chain radical[6] to initiate the other monomer polymerization. Imoto et al.[7] prepared styrene–vinyl acetate block copolymer. But in that work, only tetraethyl thiuram disulfide was used to initiate styrene polymerization, and the copolymerization conditions of polystyrene with vinyl acetate were not considered.

This work presents the results of styrene polymerization initiated by three organic disulfides and copolymerization of polystyrene terminated with an organic sulfide group with vinyl acetate. The copolymer was characterized and copolymerization conditions were considered.

EXPERIMENTAL

Materials

Tetraethyl thiuram disulfide (TETD) was recrystalized from ethanol; Tetramethyl thiuram disulfide (TMTD) and 2,2-dithiobisbenzothiazole (DM) were recrystallized from chloroform, respectively. Styrene and vinyl acetate were purified with the same methods reported previously.[8]

Preparation of Polystyrene Terminated with Organic Sulfide Group (T-PST)

Styrene bulk polymerizations initiated by three organic disulfides (TETD, TMTD, DM) were carried out at 80°C or 160°C in vacuum. After several hours, the reaction mixture was poured into a large amount of methanol to isolate the polymer. The obtained polystyrene was washed thoroughly with methanol, reprecipitated three times from benzene and methanol to remove the unreacted initiator, and dried completely in vacuum.
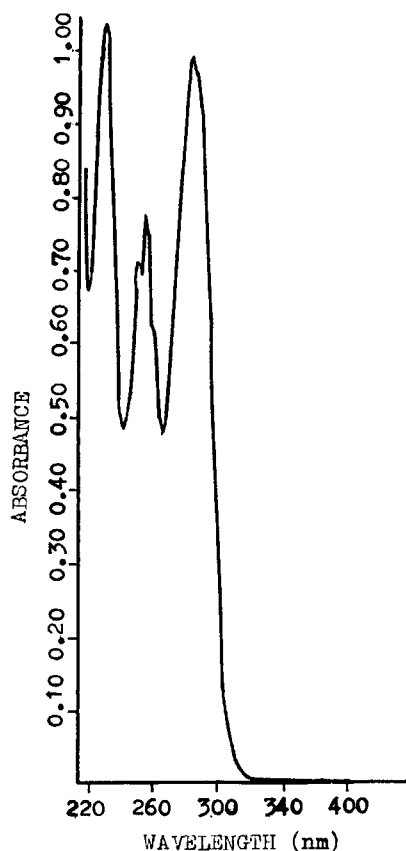
Figure 1 UV spectrum of methyl diethyldithiocarbamate in cyclohexane.

The organic sulfide group content ($\bar{X}_n$) was determinated by UV and $\bar{M}_n$ similar to the work of Otsu et al.,[9] the average number molecular weight ($\bar{M}_n$) measured by VPO.

Photopolymerization of Vinyl–Acetate with Polystyrene Ended with an Organic Sulfide Group

Styrene–vinyl acetate block copolymer was prepared by photopolymerization of vinyl acetate in the presence of T-PST as photosensitizer. Purified benzene was added to a given amount of T-PST in a hard glass tube or in a quartz cell. After T-PST was completely dissolved, vinyl acetate was added. The tube was then degassed under vacuum by the usual freezing and thawing technique prior to sealing and the quartz cell was deoxygenated by argon flow.

Photopolymerization was performed under a high-pressure mercury lamp. After a given time, the reaction mixture was poured into a large amount of petroleum ether. The isolated mixture was first extracted with methanol in a Soxhlet extractor. The existence of polyvinyl acetate (PVAc) was confirmed by UV absorption of methanol extraction solution. The extraction was continued until no absorption of PVAc was observed. After the extraction was completed, PVAc was obtained by evaporation of the methanol extraction solution. The remaining mixture was then extracted with cyclohexane. This
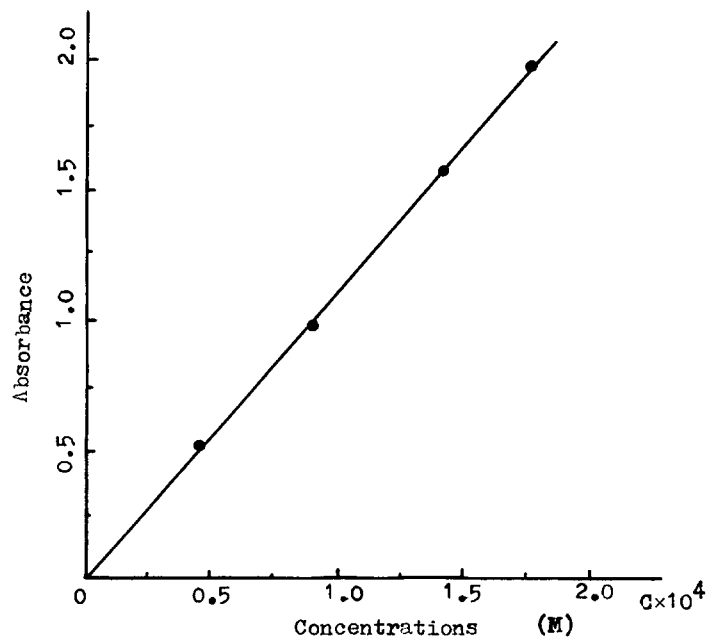

Figure 2 Curve of absorbance (A) of the model compound as a function of concentration.

Table I Results of Styrene Polymerization Initiated by TETD at 80°C for 8 h

TETD	T-PST(E)[a]	Polymer (%)	$[\eta]$	$\overline{M_n} \times 10^{-4}$	$\overline{X_n}$
0.1523	T-PST-3(E)	54.4	0.33	0.58	0.54
0.2967	T-PST-1(E)	62.2	0.29	1.59	1.12
0.4030	T-PST-4(E)	46.5	0.22	1.04	0.83
0.4557	T-PST-2(E)	44.5	0.40	0.96	0.55

Styrene: 80 mL.
[a] T-PST(E): polystyrene terminated with diethyl dithiocarbamate.

extraction was similar to the work of Shi et al.[3] and Imoto et al.[7] The unreacted T-PST was obtained by evaporation of the cyclohexane solution. The remaining polymer was dried in vacuum at 60°C for 6 h. Conversion was calculated from the weight of the dry copolymer obtained.

RESULTS AND DISCUSSION

Determination of the Absorbancy Index (ϵ) of the Model Compound (Methyl Diethyl Dithiocarbamate)

Methyl diethyl dithiocarbamate was prepared according to the method of Holloway and Gitlitz.[10] The UV spectrum of this model compound in cyclohexane showed the typical absorbance at 282 nm (Fig. 1).

Figure 2 showed the absorbance (A) of the compound at different concentrations. The absorbancy index (ϵ 1.14 × 10⁴ L/mol·cm) was thus determined.

Preparation of T-PST

Determination of the End Group Content ($\overline{X}_n$) in T-PST

Suppose that $\overline{X}_n$ is the end group content, A is the absorbance of T-PST in cyclohexane solution at 282

nm, and W is the weight of T-PST, V is the volume of solution, then the $\overline{X}_n$ value can be calculated according to the following formula:

$$\overline{X}_n = A \cdot V \cdot \overline{M}_n / b \cdot W \cdot \epsilon.$$

$\overline{M}_n$ is the average number molecular weight of T-PST.

Effect of the Amount of TETD on Styrene Polymerization

Table I is the result of styrene bulk polymerization initiated by TETD. It can be seen that the $\overline{M}_n$ value has a maximum with the increasing amount of TETD as does the $\overline{X}_n$ value. This can be explained by the fact that TETD has a mild ability to initiate styrene polymerization. When a larger amount of TETD is used, it may have a retarding effect on polystyrene chain propagation.

Effect of the Three Initiators on Styrene Polymerization

Table II contains the results of styrene polymerization. It shows that the order of initiating abilities of the three organic disulfides is TETD > TMTD > DM. This is caused by the decomposition of the organic disulfides: the more easily the initiator decomposes, the stronger its initiating ability is.

Table II Effect of Different Initiators on Styrene Polymerization

Initiator	Amount (g)	Temperature (°C)	Time (h)	Polymer (%)	$[\eta]$	$\overline{M_n} \times 10^{-4}$	$\overline{X_n}$
TETD	0.2967	80	8	62.2	0.29	1.59	1.12
TMTD	0.2419	80	8	41.0	0.23	0.96	0.92
DM	0.3312	106[a]	5	46.3	0.27	1.45	1.4[b]

Styrene: 30 mL.
[a] No polymerization was obtained at 80°C, result attained at 106°C.
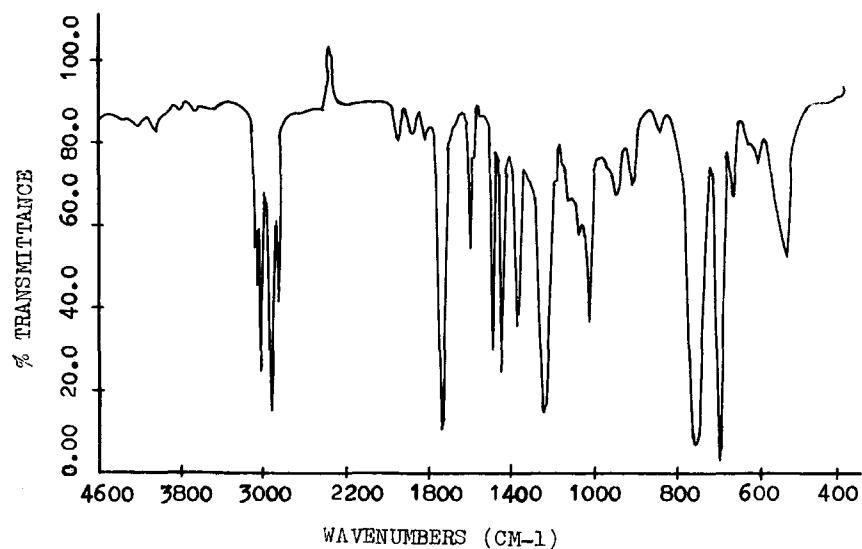[b] The model compound is methyl thiobenzothiazole.

Figure 3   IR spectrum of styrene–vinyl acetate block copolymer.

Preparation of Styrene–Vinyl Acetate Block Copolymer

Characterization of Styrene–Vinyl Acetate Block Copolymer

IR spectrum of the block copolymer examined with a thin film is shown in Figure 3. Intense absorption bands of the phenyl group appeared at 700 cm^{-1} and 758 cm^{-1}, and those of the carboxide of acetate group at 1740 cm^{-1}.

^{1}H-NMR spectrum of the block copolymer was obtained in CDCl$_3$ (Fig. 4). It shows the existence of the proton resonance of methyl of acetate at 2.01 ppm. Protons of the phenyl group, because of the
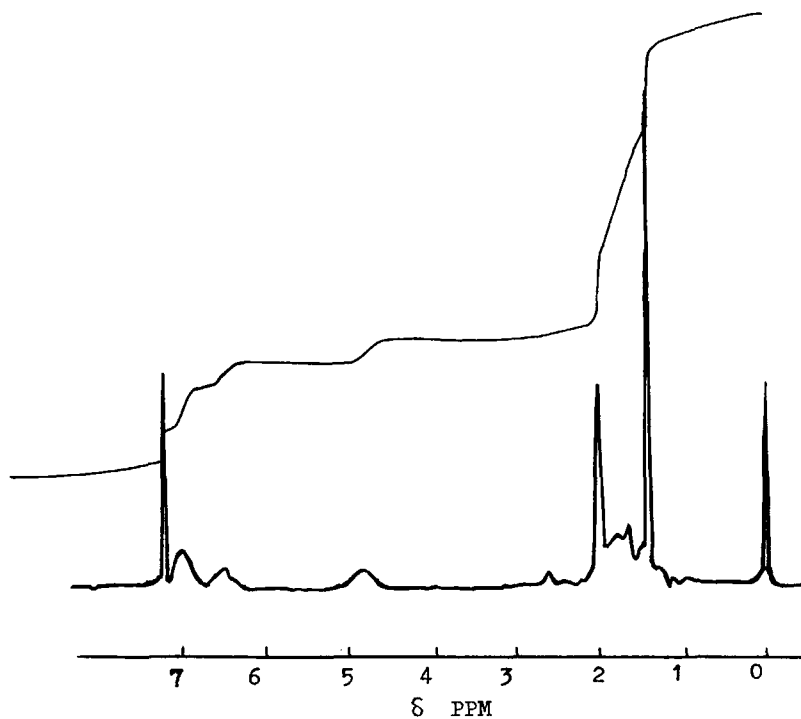

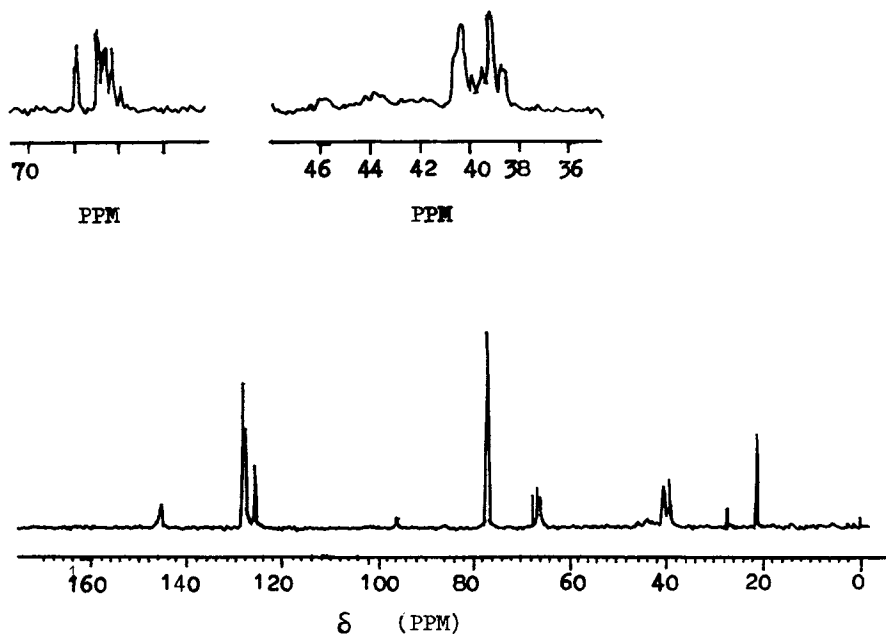**Figure 4** ^{1}H-NMR spectrum of styrene–vinyl acetate block copolymer.

Figure 5 ^{13}C-NMR spectrum of styrene–vinyl acetate block copolymer.

different chemical environment, split into two res-
onance sites: *ortho*-protons resonate at 6.5 ppm, and
the *para*- and *meta*-protons appear at 7.0 ppm. The
composition of the copolymer was thus calculated

based on the integral area of protons in the acetate
and phenyl groups.

Figure 5 is the ^{13}C-NMR spectrum of the copol-
ymer. The carbon of carboxide resonates at 170 ppm,

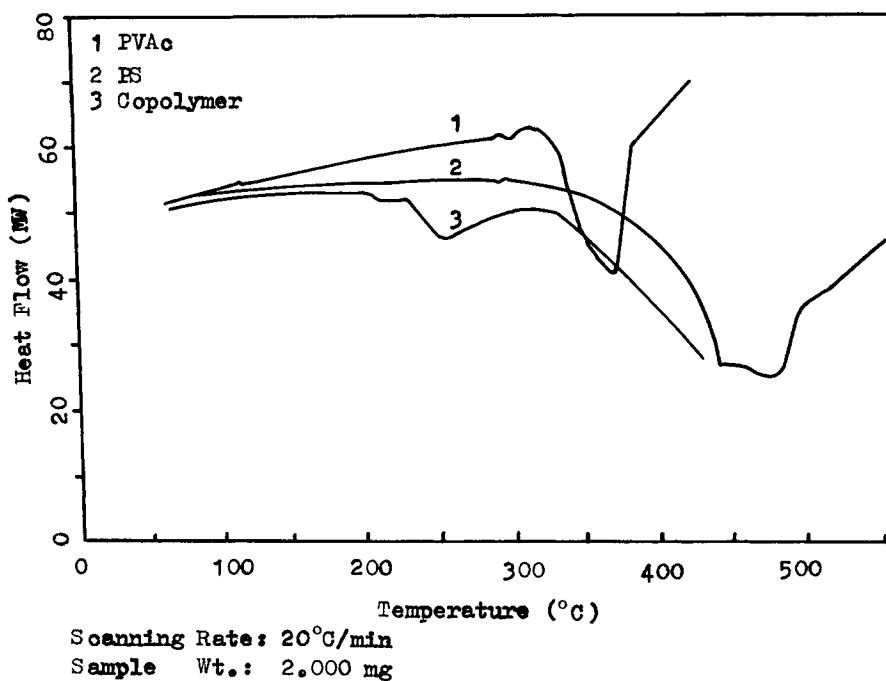Scanning Rate: 20°C/min
Sample   Wt.: 2.000 mg

Figure 6 Thermogram of polymer: (1) polyvinyl acetate; (2) polystyrene; (3) styrene–
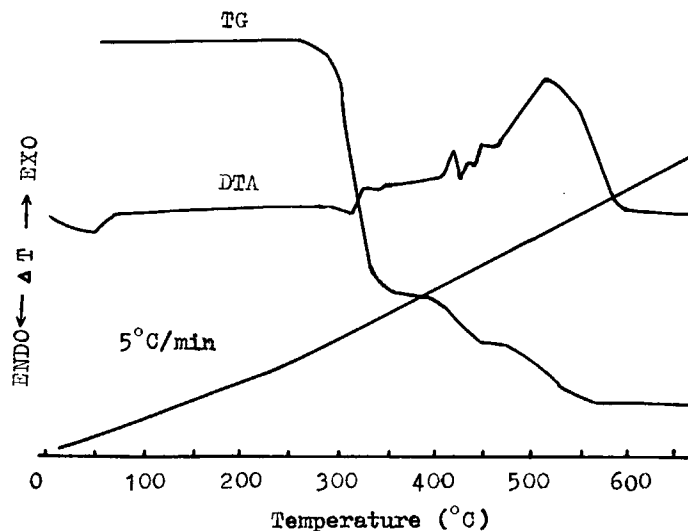vinyl acetate block copolymer.

Figure 7 Thermogram of polyvinyl acetate.

carbons of the phenyl group and acetate group appear at 125–127 and 21 ppm, respectively.

IR. NMR spectra confirm that the obtained copolymer has not only a phenyl group but an acetate group also. In order to further identify the copolymer, thermoanalyses were employed.

Figure 6 is the thermogram of PVAc, polystyrene (PS) and styrene–vinyl acetate block copolymer (V-

b–S). Obviously the decomposition temperature of the copolymer is below that of PVAc or PS.

Figure 7–9 are thermograms of PVAc, T-PST, and V–b–S, respectively. From these thermograms it can be concluded that the copolymer has both components of styrene and vinyl acetate chain parts.

TEM Characterization. Figure 10 is the TEM photograph of the ultrathin film of styrene–vinyl acetate

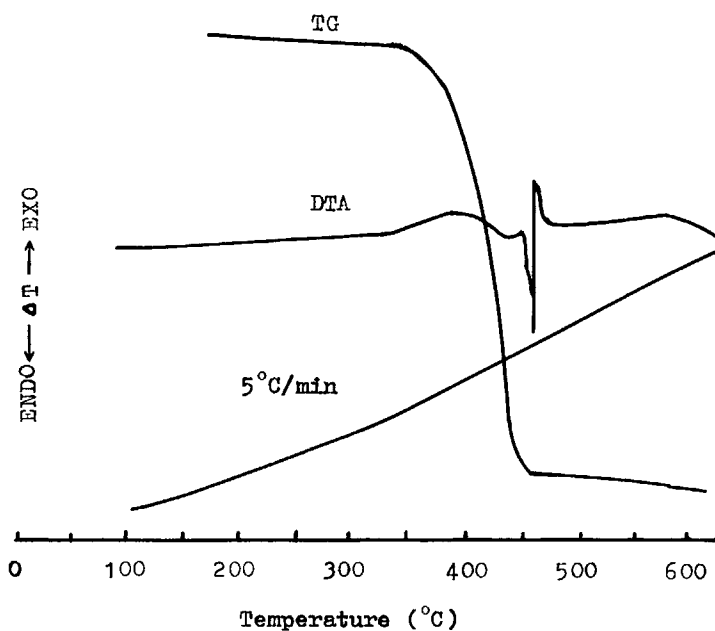

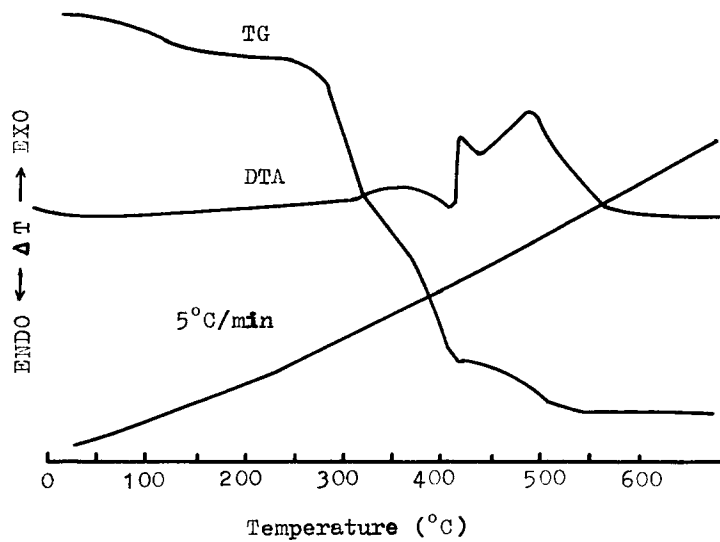**Figure 8** Thermogram of polystyrene terminated with diethyldithiocarbamate.

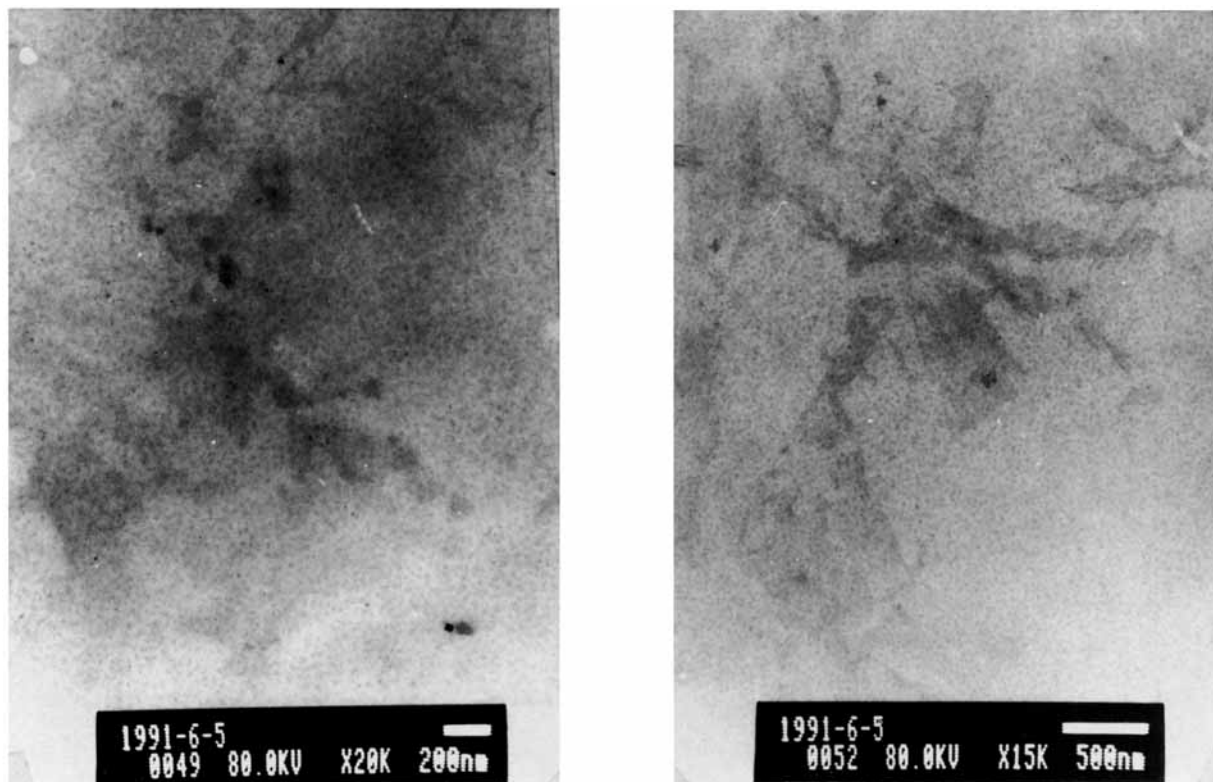**Figure 9**   Thermogram of styrene–vinyl acetate block copolymer.

Figure 10   TEM photograph of the ultrathin film of styrene–vinyl acetate block copolymer.

Table III   T-PST-1(E)

Amount (g)	PVAc (g)	Recovered PS (g)	Copoly- mer (g)	$[\eta]$	VAc (%)
1	0.1512	0.2492	1.3294	0.54	55.7
2	0.0925	0.5435	2.6349	0.40	44.7
3	0.5450	1.0129	3.7648	0.40	27.1

Benzene: 10 mL; VAc: 20 mL; time: 5 h. $[\eta]$ = 0.29.

Table V   T-PST(DM)

Amount (g)	PVAc (g)	Recovered PS (g)	Copoly- mer (g)	$[\eta]$	VAc (%)
1	0.1052	0.2352	1.2173	0.45	32.8
1.5	0.2925	0.6279	1.0418	0.32	17.2

Benzene: 15 mL; VAc: 20 mL; time: 5 h. $[\eta]$ = 0.27.

copolymer. Microphase separation can be observed. This indicates that the obtained copolymer is block copolymer.

Effect of Reaction Conditions on Copolymerization

Amount of T-PST on Copolymerization. Tables III–V are the results of copolymerization using T-PST as initiators. More vinyl acetate chain parts can be introduced into the copolymer chain with a lesser amount of T-PST used. Results of copolymerization are listed in Table VI with a fixed amount of VAc and concentration of the organic sulfide group.

The introduced VAc chain parts in the copolymer decrease according to the order of T-PST(E), T-PST(M), and T-PST(DM). This shows that the initiating order of T-PST is T-PST(E) > T-PST(M) > T-PST(DM). This might be caused by the breakage of the C — S bond. The more easily the organic sulfide group breaks, the stronger the initiating ability of T-PST is.

Reaction Time on Copolymerization. Table VII shows that more VAc chain parts can be introduced into the copolymer chain with increased time. Earlier work[11] presented the concept of iniferter (initiator–transfer–terminator), and pointed out that TETD is a good iniferter for styrene bulk polymerization. Virtually, if the polymer ended with a func-

tional group that could break into the polymer chain radical that has initiating activity and a small radical with less or no initiating ability, the polymer chain could propagate further with increased time, and the polymerization proceeds via a living radical mechanism.

As far as this copolymerization is concerned, more vinyl acetate chain parts could be introduced into the copolymer chain with increased time. Moreover, only a small amount of polyvinyl acetate could be obtained. This indicates that the diethyldithio radical $[(C_2H_5)_2NCSS—]$ produced by the breakage of T-PST is comparatively stable, and the polystyrene chain radical has the activity of initiating vinyl acetate. Thus, the copolymerization proceeds via living radical mechanism.

$$—(CH_2—\overset{|}{\underset{C_6H_5}{C}}H)_n—CH_2—\overset{|}{\underset{C_6H_5}{C}}H—R \xrightarrow{\text{high pressure mercury lamp}}$$

$$R^\bullet + —(CH_2—\overset{|}{\underset{C_6H_5}{C}}H)_n—CH_2—\overset{|}{\underset{C_6H_5}{C}}H^\bullet \xrightarrow{mCH_2=CHOCOCH_3}$$

$$—(CH_2—\overset{|}{\underset{OCOCH_3}{C}}H)_m—(CH_2—\overset{|}{\underset{C_6H_5}{C}}H)_n—CH_2—\overset{|}{\underset{C_6H_5}{C}}H—R \rightleftharpoons$$

$$\longrightarrow \cdots\cdots R=S—\overset{\|}{\underset{S}{C}}—\overset{|}{\underset{C_2H_5}{N}}—C_2H_5$$

$$S—\overset{\|}{\underset{S}{C}}—\overset{|}{\underset{CH_3}{N}}—CH_3 \quad S—\overset{N}{\underset{S}{\diagup}}$$
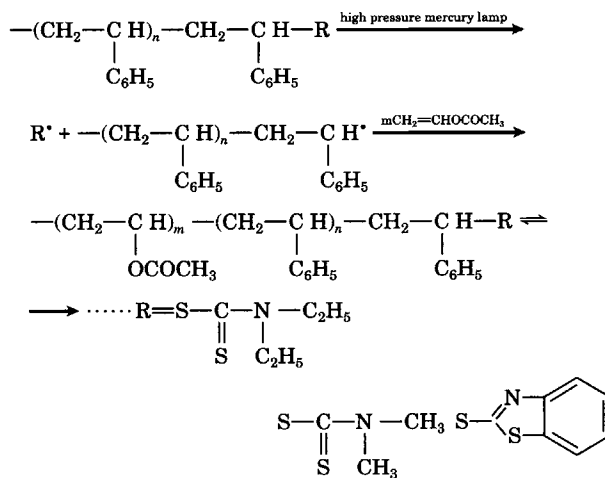
Table IV   T-PST(M)

Amount (g)	Benzene (mL)	PVAc (g)	Recovered PS (g)	Copolymer (g)	$[\eta]$	VAc (%)
1	10	0.1425	0.3047	0.8837	0.33	39.1
1.5	10	0.1520	0.5192	1.1243	0.29	26.6
2	15	0.1162	0.2399	1.6539	0.32	33.9

VAc: 20 mL; time: 5 h. $[\eta]$ = 0.23.

Table VI   Effect of Different End Groups on Copolymerization

T-PST	$[\eta]$	Conc. (M)	PVAc (g)	Recovered PS (g)	Copolymer (g)	$[\eta]$	VAc (%)
T-PST-1(E)	0.29	7.0×10^{-3}	0.1512	0.2492	1.3297	0.54	55.7
T-PST(M)	0.23	7.2×10^{-3}	0.1425	0.3047	0.8837	0.33	39.7
T-PST(DM)	0.27	6.6×10^{-3}	0.1052	0.2352	1.2173	0.45	32.8

VAc: 20 mL; time: 5 h.

Table VII   Effect of Reaction Time on Copolymerization

Time (h)	PVAc (g)	Recovered PS (g)	Copolymer (g)	$[\eta]$	VAc (%)
3	0.1640	0.3520	0.7568	0.39	52.2
5	0.1242	0.3050	1.0638	0.41	50.0
8	0.1032	0.2934	1.8241	0.41	58.9
12	0.0976	0.2756	2.3801	0.52	67.6

T-PST-4(E): 1 g; VAc: 20 mL; benzene: 10 mL.

Since this copolymer is obtained by the technique of step-by-step chain propagation, and the inherent viscosity of copolymer increases with time, together with the former characterizations, copolymer can be further proved to be block copolymer.

Effects of the End Group Content ($\bar{X}_n$) on Copolymerization. Table VIII is the result of the effect of $\bar{X}_n$ value on copolymerization. More vinyl acetate chain parts can be introduced into the copolymer chain when $\bar{X}_n$ is ~ 1, however, when $\bar{X}_n$ is ~ 0.5, contrary results were obtained. For example, when $\bar{X}_n$ is 0.55, the introduced VAc chain parts cannot increase with increased time, that is, the copolymerization cannot proceed well via a living radical mechanism. It indicates that the $\bar{X}_n$ value is a key factor for the copolymerization.

Effects of Reaction Vessels on Copolymerization. The results of copolymerization obtained by sealed glass tube and quartz cell are listed in Table IX. More vinyl acetate chain parts could be introduced into the copolymer chain that used the quartz cell as the

Table VIII   Effects of the $\bar{X}_n$ Value on Copolymerization

T-PST(E)[a]	$[\eta]$	$\bar{X}_n$	PVAc (g)	Recovered PS (g)	Copolymer (g)	$[\eta]$	VAc (%)
T-PST-1(E)	0.29	1.12	0.1512	0.2492	1.3297	0.54	56.7
T-PST-4(E)	0.22	0.83	0.1242	0.3050	1.0635	0.41	50.0
T-PST-2(E)	0.40	0.55	0.1260	0.2682	0.7355	0.56	11.8
T-PST-3(E)	0.33	0.54	0.1350	0.2875	0.8757	0.41	25.7

VAc: 20 mL; benzene: 10 mL; reaction time: 5 h.
[a] T-PST(E): polystyrene terminated with diethyl dithiocarbamate.

Table IX   Results of Copolymerization Obtained by Different Reaction Vessels

$\bar{X}_n$ of T-PST	Reaction Vessel	PVAc (g)	Recovered PS (g)	Copolymer (g)	VAc (%)	Solubility[a]
0.83	Glass tube	0.1242	0.3050	1.0635	48.4	Soluble
	Quartz cell	0.9053	0.3758	1.4043	55.6	Partially soluble
0.55	Glass tube	0.1260	0.2682	0.8757	11.8	Soluble
	Quartz cell	1.0423	0.7562	1.0435	35.8	Partially soluble

T-PST: 1 g; benzene: 10 mL; VAc: 20 mL.
[a] The solubility was tested in benzene and chloroform, respectively.

reaction vessel. However, the obtained copolymer is partially insoluble in benzene and in chloroform. This might be because of the reaction vessels, more light quanta could be absorbed by the reaction mixture in quartz. Since the polymerization of vinyl acetate initiated by UV light is an exothermic reaction, once the polymerization begins, it may be accelerated by itself. The cross-linking structure that makes the copolymer insoluble might be produced by chain transfer reaction.

CONCLUSIONS

Methods that permitted the copolymerization of styrene with vinyl acetate were developed. The procedure included two stages:

1. Preparation of polystyrene ended with organic sulfide group initiated by three organic disulfides.
2. Preparation of styrene–vinyl acetate block copolymer by the copolymerization of polystyrene ended with an organic sulfide group and vinyl acetate.

Results reveal that the end group content in polystyrene is a key factor for the copolymerization. By

controlling the reaction conditions, a different composition (VAc %) of copolymer could be obtained.

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