Controllable Radical Copolymerization of Styrene and Methyl Methacrylate Using 1,1,2,2-Tetraphenyl-1,2-bis(trimethylsilyloxy) Ethane as Initiator

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ABSTRACT: Copolymerization of styrene (St) and methyl methacrylate (MMA) was carried out using 1,1,2,2-tetraphenyl-1,2-bis (trimethylsilyloxy) ethane (TPSE) as initiator; the copolymerization proceeded via a "living" radical mechanism and the polymer molecular weight (M_w) increased with the conversion and polymerization time. The reactivity ratios for TPSE and azobisisobutyronitrile (AIBN) systems calculated by Finemann–Ross method were $r_{St} = 0.216 \pm 0.003$, $r_{MMA} = 0.403 \pm 0.01$ for the former and $r_{St} = 0.52 \pm 0.01$, $r_{MMA} = 0.46 \pm 0.01$ for the latter, respectively, and the difference between them and the effect of polymerization conditions on copolymerization are discussed. Thermal analysis proved that the copolymers obtained by TPSE system showed higher sequence regularity than that obtained by the AIBN system, and the sequence regularity increased with the content of styrene in copolymer chain segment. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1474–1482, 2001

Key words: controllable radical copolymerization; styrene; methyl methacrylate; 1,1,2,2-tetraphenyl-1,2-bis (trimethylsilyloxy) ethane

INTRODUCTION

A notable feature of radical polymerization is its wide suitability for the monomers. In most cases, however, the chain propagation of radical polymerization is hard to control and chain structure is random. In the last ten years, significant advances have been made in controllable radical polymerization. The Atom Transfer Radical Polymerization (ATRP),[1] nitroxyl-mediated[2] radical polymerization system are used efficiently to prepare polymers with well-defined structure and controlled molecular weight. But for ATRP a large amount of catalysts should be used and it is very difficult to be removed after polymerization, and for nitroxyl-mediated radical polymerization, some common monomers, such as methacrylic acid and its corresponding ester, cannot been used,[2] so its application is limited.
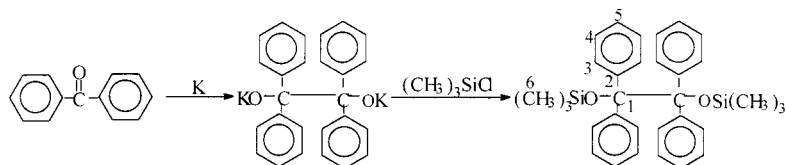
The 1,1,2,2- tetraphenyl-1,2-bis (trialkylsilyloxy) ethane (TPSE) is a another kind of radical thermal initiator. At 80–130°C, its C—C bond is easily broken, yielding a pair of trimethylsilyloxy-diphenyl methyl radicals (TMSDM ·) that are

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Scheme 1

relatively stable due to resonance effect. It can initiate methyl methacrylate (MMA) and styrene (St) to polymerize by reversible deactivation[3–5] or degenerative transfer mode[6] of growing polymeric radicals with diphenylmethyl radicals.

This paper describes the controlled copolymerization of MMA and St mediated by TPSE-based initiating systems. The differences of relative reactivity ratios of MMA and St for TPSE and AIBN systems were discussed.

EXPERIMENTAL

Materials

MMA and St was dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. Chlorotrimethylsilane (Shanghai Qingpu Synthetic Reagent Factory) was distilled on molecular sieve and collected in a burette. Benzophenone (Beijing Chem-

ical Reagent Factory, China) was recrystallized twice from ethanol. All other reagents were purified by common drying and distillation procedures.

Preparation of Initiator

TPSE was synthesized by dimerization of benzophenone according to the literature[7] (Scheme 1); the mp of purified product: 132–133°C.

Characterization: ^{13}C NMR (δ: ppm): 2.45 (C_6), 88.37 (C_1), 125.76 (C_3), 126.34 (C_5), 131.14 (C_4), 145.65 (C_2). IR (cm^{-1}): 1597, 1491, 752 (benzene ring); 1250, 830 (Me$_3$Si); 1105 (C—O—Si).
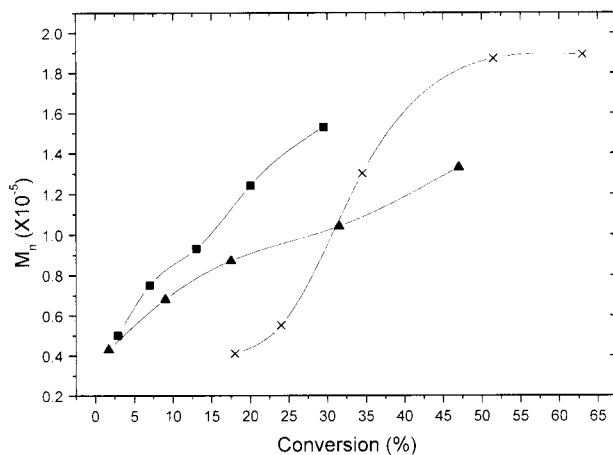
Copolymerization

In 100 mL ampoule contained definite amount of TPSE or AIBN the required quantities of monomers were introduced, then degassed under vacuum. Copolymerization was run at a precisely controlled temperature for the given time. In the

Table I   Copolymerization Data for St (M_1) with MMA (M_2) in Bulk^a

| T (°C)	$[M]_0{}^a/[I]_0{}^b$	Reaction Time (min)	M_n ($\times 10^{-5}$)	M_w/M_n	Conversion (%)
90	100	15	0.50	1.92	2.9
		25	0.75	1.90	7.0
		45	0.93	1.86	13.0
		65	1.24	1.90	20.0
		85	1.53	1.91	29.5
90	50	10	0.43	2.04	1.7
		20	0.68	2.01	9.0
		35	0.87	2.08	17.5
		60	1.04	2.06	31.5
		75	1.33	2.01	47.0
120	50	17	0.41	2.10	18.0
		30	0.55	2.21	24.0
		45	1.30	1.98	34.5
		60	1.87	2.31	51.5
		75	1.89	2.07	63.0

^{a} $[M]_0$: initial monomer concentration; $[I]_0$: concentration of TPSE.
^{b} Copolymerization condition: monomer feed ratio (mol/mol) : [St] : [MMA] = 1 : 1.

Figure 1 Relationship of M_n with conversion (copolymerized with TPSE initiator system ([St]:[MMA]:[TPSE] = 50:50:1) in bulk. (■) [Monomer]$_0$:[TPSE]$_0$ = 100:1, copolymerization temperature: 90°C; (▲) [Monomer]$_0$[TPSE]$_0$ = 50:1, copolymerization temperature: 90°C; (×) [Monomer]$_0$:[TPSE]$_0$ = 50:1, copolymerization temperature: 120°C.

experiment at 120°C, nitrogen is induced to keep a pressure to prevent the boiling of MMA. The reaction mixture was then diluted with chloroform and the copolymer was precipitated in large amount of petroleum ether (30–60°C). The remaining monomers could be removed from the copolymer by the dissolving and precipitation procedure using chloroform/petroleum (30–60°C).
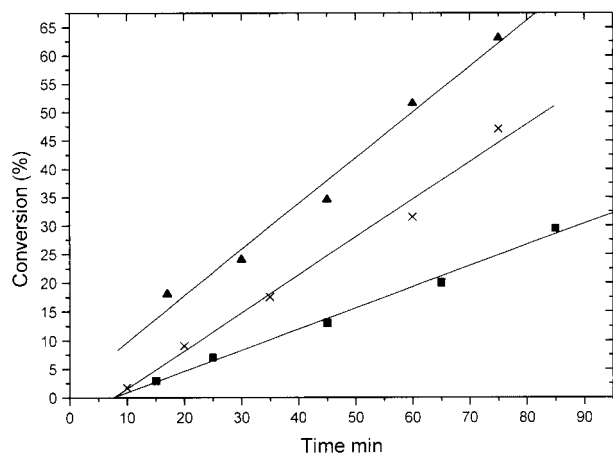
Figure 2 Relationship of conversion with copolymerization time. (■) [Monomer]$_0$:[TPSE]$_0$ = 100:1, copolymerization temperature: 90°C; (×) [Monomer]$_0$:[TPSE]$_0$ = 50:1, copolymerization temperature: 90°C; (▲) [Monomer]$_0$:[TPSE]$_0$ =50:1, copolymerization temperature: 120°C.
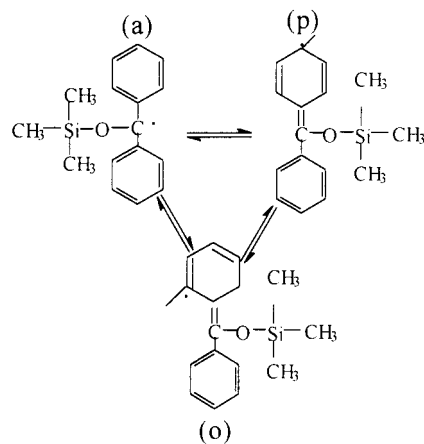
Scheme 2

After that, the copolymer were rinsed with petroleum ether (30–60°C) in a Soxhlet extractor for 24 h, and then dried under vacuum at 40–50°C for 48 h.

Measurement

^{1}H NMR was recorded on a Bruker MSL-300 spectrometer with tetramethylsilane as internal standard and CDCl$_3$ as solvent. The number-average molecular weight of the copolymers was derived with a Shimadzu LC-3A gel permeation chromatograph (GPC) using refractive index as detector: column length, 1.2 m; filler, crosslinking polystyrene gel (1250 mesh), injection volume, 1 mL (concentration: 0.1 g/mL); solvent and eluent, chloroform; flow rate, 1.0 mL/min; pump pressure, 40 kg/cm^2 (3.99×10^6 Pa). Monodistribution polystyrene was used as a standard sample. Thermogravimetric data (TGA) were obtained using NETZSCH TG 209 thermal analyzer in a nitrogen atmosphere at heating rate of 10°C/min. Differential scanning calorimetry (DSC) studies were conducted with a SETARAM-DSC92 in a nitrogen atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Controllability of Copolymerization

Table I gives the data of the copolymerization in the presence of TPSE. The molecular weight of the copolymers increases with the total conver-

TMSDM 〜〜〜〜$_m$ MDSMT ⇌ TMSDM 〜〜〜〜$_m$· + ·MDSMT

TMSDM· : $(CH_3)_3-Si-O-\underset{}{\overset{}{C}}·$
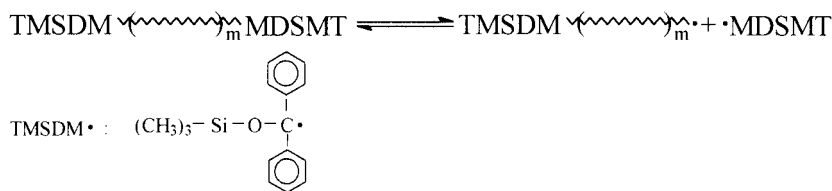
Scheme 3

sion (Fig.1), which shows the basic properties of the "living" radical polymerization.

However, Figure 2 indicates that there exists an induction period for The PSE system, it lasts about a few minutes, and moreover, the higher the concentration of TPSE, the longer the induction period. Santos et al.[8] also found a similar phenomenon in the investigation of St polymerization in the presence of TPSE.

It is well known that TPSE is easy to decompose, its half-life of decomposition at 70°C is only a few seconds,[8] and obtained trimethylsilyloxydiphenyl methyl radical (TMSDM ·) can react with monomers to form the primary radicals, Lankamp[9] suggested that the three semibenzopinacol radicals in Scheme 2 also might be formed when the TPSE decomposed, in which only radical (a) could constitute reversible termination with propaga-

tion species, and radicals (p) and (o) would constitute irreversible termination when it coupled with propagation species. At the beginning of initiation, radical concentration is much high, nearly all primary radical are terminated by radicals (p), (o), and (a) as soon as it is formed. Thus the polymerization is inhibited, and no polymer was formed in this time, which caused the induction period.

At the end of induction period, as the concentration of copolymer with TMSDM end groups increases, and the concentration of TMSDM · drops, the equilibrium in Scheme 3 would turn to the right; then the copolymerization is conducted on the "living radical mechanism" due to reversible termination of TMSDM · . But during the polymerization process, the mesomerism of TMSDM · makes the polymerization lose this "liv-
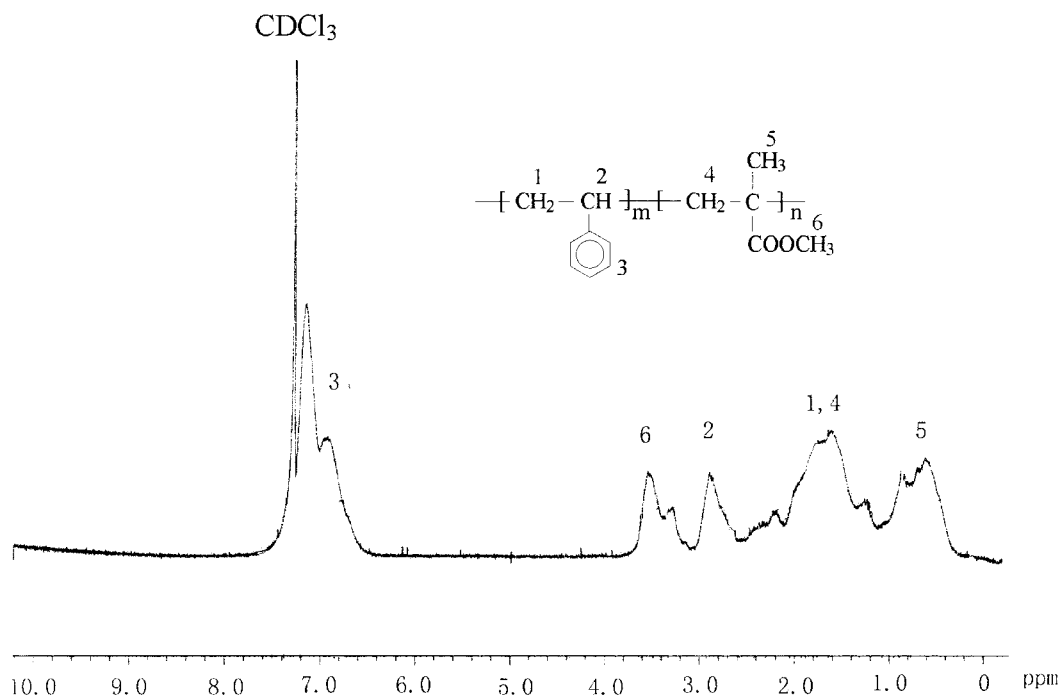
Figure 3 ^{1}H NMR spectrum of poly(St-co-MMA) (M_n = 75,000 and M_w/M_n = 1.89) synthesized with PPSE initiator ([St]:[MMA]:[TPSE] = 50:50:1) in bulk at 100°C.
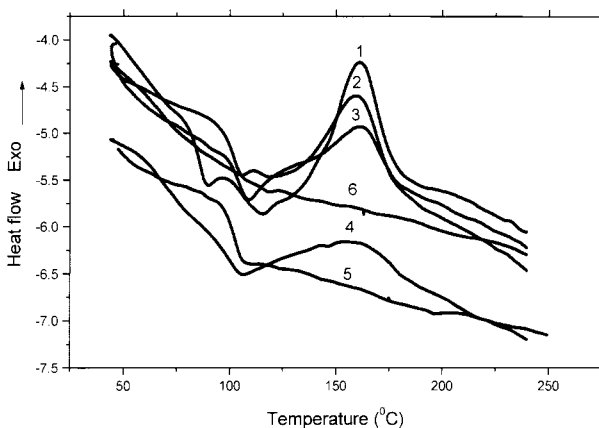
Figure 4 DSC curve of copolymers. Feed ratio of St/MMA (mol/mol): 1.80:20, 2.60:40, 3.50:50, 4.4:60, and 5.20:80 for TPSE, and 6.5:50 for AIBN; copolymerization temperature: 100°C; time: 25 min; [Monomer]$_0$: [TPSE]$_0$ = 100:1.

ing" property, so the molecular weight distribution is widened.

Comparison of the Monomer Reactivity Ratio of TPSE to AIBN System

The copolymerizations of styrene and MMA in the presence of TPSE are performed at varying feed monomer ratios, and Figure 3 is a typical ^{1}H NMR spectrum of product. The copolymer compositions are calculated by the integrated areas of peculiar peaks of the St and MMA unit in the copolymer using the following equation:

$$\frac{m_1}{m_2} = \frac{A_1 \times 1/5}{(A_2 - A_1 \times 8/5) \div 8}$$

Here m_1 and m_2 are the mole fraction of styrene and MMA in copolymer, respectively, and A_1 is the integrated area of the phenyl protons of styrene unit at 6.5–7.5ppm and A_2 is the integrated area of the all protons of the copolymer. The monomer reactivity ratios are calculated by Finemman–Ross method[10] from the data in Figure 2 and Figure 4, and r_{St} = 0.216 ± 0.003, r_{MMA} = 0.403 ± 0.01 for TPSE system and r_{St} = 0.52 ± 0.013, r_{MMA} = 0.46 ± 0.01 for AIBN, the difference for both cases is observed.

In the AIBN initiator system, it is found that the reactivity ratios of St and MMA are only dependent on the reaction rate constant between chain radicals and monomers.[11] However, for the TPSE system, the structure of monomer would exert strongly effect on the copolymerization due to stereo effect of the TMSDM group in the propagation chain end. It is obvious that the St with large phenyl ring is not easy to add to the propagation chain end comparing with the MMA. Therefore for TPSE system the homopolymerization rate constant of MMA (k_{MMA} = 4.2 × 10^{-3} mol s^{-1} L^{-1} at 100°C)[5] is greater than that of the St (k_{St} = 1.4 × 10^{-3} mol s^{-1} L^{-1}, at 100°C),[8] so r_{MMA} increases and r_{St} decreases.

Effect of Monomer Feed Ratio on the Copolymerization

It is observed that there are some unusually characterics for this system shown in Table II; the total monomer conversion and molecular weight of the copolymer decrease but the molecular weight distribution is widened with the increase of St in the monomer feed ratio. For example, in Table II when the St content in feed ratio is 20

Table II   Effect of Feed Ratio on the Copolymerization in Bulk^a (TPSE)

Feed Ratio (mol/mol)		Conv. (%)	R_p^b (mol · l^{-1} · s^{-1})	Copolymer Composition		M_n (×10^{-5})	M_w/M_n
St	MMA			St (mol %)	MMA (mol %)		
20	80	10.8	0.54	29.1	70.9	0.96	1.54
40	60	7.7	0.50	42.2	57.8	0.79	1.87
50	50	6.8	0.48	45.9	54.1	0.75	1.89
60	40	6.0	0.46	51.0	49.0	0.68	1.91
80	20	5.6	0.41	62.9	37.1	0.49	1.78

^{a} Copolymerization conditions: temp.: 100°C; time: 25 min; [Monomer]$_0$/[TPSE]$_0$ (mol/mol) = 100 : 1.
^{b} R_p is defined as

$$R_p = \frac{-d([M_1] + [M_2])}{dt}/(I^{1/2}/\delta_1)$$

$$\text{TMSDM} \sim\sim\sim\sim_{n\text{-}1}\text{MMA} - \text{MDSMT} \xrightarrow{\text{heat}} \text{TMSDM} \sim\sim\sim\sim_{n\text{-}1}\text{MMA} \cdot + \cdot \text{MDSMT}$$

$$\downarrow \text{MMA}$$

$$\text{TMSDM} \sim\sim\sim\sim_{n+1}\text{MMA} - \text{MDSMT}$$

$$\text{TMSDM} \cdot \quad (\text{CH}_3)_3 - \text{Si} - \text{O} - \text{C} \cdot$$
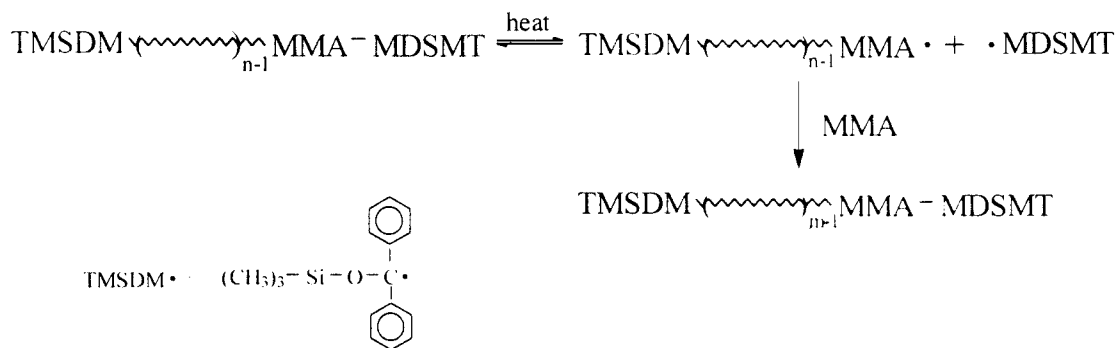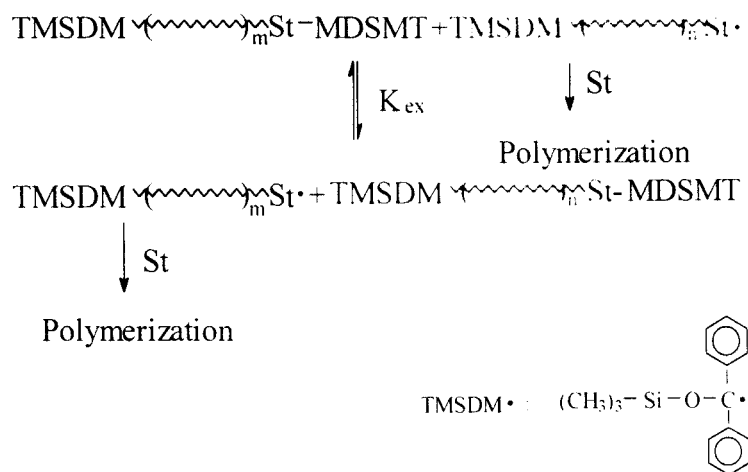
Scheme 4

mol %, the monomer conversion is 10.8%, the molecular weight is 9.6×10^4 and the molecular weight distribution is 1.54 after polymerization for 15 min at 90°C. However, in the same conditions, the monomer conversion decreases to 5.6, the molecular weight drops to 4.9×10^4 and molecular weight distribution turns to 1.78 when the St content in feed ratio increases to 80 mol %.

As we well know, in the TPSE system, the addition mode of St is different from the MMA. For the MMA homopolymerization system, the monomer addition is carried out by the reversible termination between growing chain radicals, and TMSMD · , and MMA monomers are inserted at the intermediate between growing chain radicals and TMSMD · shown in Scheme 3. However, the St polymerization, in the presence of TPSE, is conducted on the so-called degenerative transfer mechanism shown in Scheme 4, whose effective-
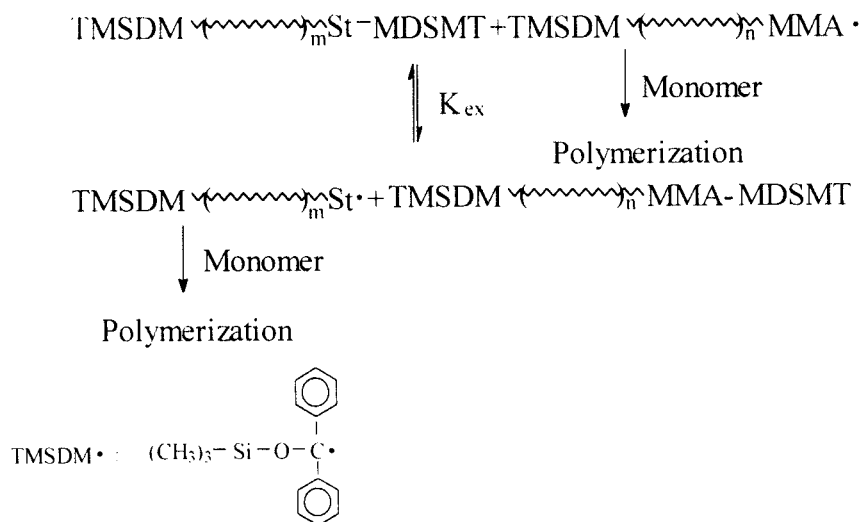
ness is mainly governed by the rate exchange constant (K_{ex}).[6]

When the copolymerization of MMA and St using TPSE as initiator is going, the situation is more complicated than that in the case of homopolymerization. In the copolymerization, TMSMD · formed by homolysis of TPSE can initiate both MMA and St to form the primary radicals, then terminate by another part of TMSMD · to form the dormant species. As we mentioned before, however, in the TPSE system only MMA is propagated via reversible termination mechanism and St is propagated by regenerative transfer mechanism after induction period. It means that when the chain radical or primary radical ended with St are terminated by TMSMD ·, they can only be activated by exchangeable reaction with the chain radicals with MMA end shown in Scheme 5, otherwise they would lost their reactivity. It is different from the St homopolymeriza-

$$\text{TMSDM} \sim\sim\sim_{m}\text{St} - \text{MDSMT} + \text{TMSDM} \sim\sim\sim_{n}\text{St} \cdot$$

$$\Big\updownarrow K_{ex} \qquad \downarrow \text{St}$$

$$\text{Polymerization}$$

$$\text{TMSDM} \sim\sim\sim_{m}\text{St} \cdot + \text{TMSDM} \sim\sim\sim_{n}\text{St} - \text{MDSMT}$$

$$\downarrow \text{St}$$

Polymerization

$$\text{TMSDM} \cdot \quad (\text{CH}_3)_3 - \text{Si} - \text{O} - \text{C} \cdot$$

Scheme 5

TMSDM ⌇⌇⌇⌇⌇)m̅ St⁻MDSMT + TMSDM ⌇⌇⌇⌇⌇)n̅ MMA ·

K_{ex} Monomer

Polymerization

TMSDM ⌇⌇⌇⌇⌇)m̅ St· + TMSDM ⌇⌇⌇⌇⌇)n̅ MMA-MDSMT

Monomer

Polymerization

TMSDM· = $(CH_3)_3$−Si−O−Ċ·

Scheme 6

tion in which although the primary radicals with St end are terminated by TMSMD · , but they can be further propagated with left chain or primary radicals with St end by exchangeable reaction. In the propagation of copolymerization, however, when the MMA is excessive in feed ratio, no free chain or primary radicals with St end can be detected because the TMSMD · radicals formed by the reversible termination of polymer chain ended with MMA are able to cap the chain or primary radicals ended with St as soon as they formed. As MMA content in the feed ratio decreases, the amount of inactive dormant species with styrene end capped by TMSMD · is more and more, so the molecular weight of the copolymer and monomer conversion drop, and the molecular weight distribution widens.

Table III   Effect of Feed Ratio on the Copolymerization in Bulk[a] (AIBN)

Feed Ratio (mol/mol)		Copolymer Composition	
St	MMA	St (mol %)	MMA (mol %)
20	80	29.1	70.9
40	60	46.1	53.9
50	50	52.8	47.2
60	40	58.4	41.6
80	20	74.1	25.9

[a] Copolymerization conditions: temp.: 100°C; time: 15 min; [Monomer]$_0$/[AIBN]$_0$ (mol/mol) = 100 : 1.

The same conclusion can also be derived from the Walling equation[12]:

$$\frac{-d([M_1] + [M_2])}{dt}$$
$$= \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)(I^{1/2}/\delta_1)}{[r_1^2[M_1]^2 + 2\phi r r_1 r_2[M_1][M_2] + r_2[M_2]^2(\delta_2/\delta_1)^2]^{1/2}}$$

Here r_1 and r_2 are the monomer reactivity ratio, δ_1, δ_2 are the ratios of the square root of the rate constants of chain termination to the chain growth for individual monomers, I represents the rate at which kinetic chains are started, ϕ depends on the rate constant of "crossed" termination and the geometric mean of the rate constants of chain termination of each monomer alone, and the value is 13 for the MMA and St systems.

Table IV   TGA Data of Copolymer

No.	St in Copolymer (mol %)	M_n (×10^4)	T_i (°C)	T_{max}[c] (°C)	T_f (°C)
A[a]	45.9	7.5	299.3	339.9	379.2
B[b]	46.1	7.3	295.7	331.1	375.7

[a] Copolymer prepared in the presence of TPSE at 90°C.
[b] Copolymer prepared in the presence of AIBN at 90°C.
[c] T_{max} was designated as the temperature of rate of maximum loss weight.

Table V   Effect of Feed Ratio on the Chain Structure of Copolymer[a]

Composition in Feed (mol %)		Copolymer Composition (mol %)		Sequence Distribution (mol %)			
				MMA-MMA (X)	St-St (Y)	MMA-St (Z)	Enthalpy (mJ/mg)
MMA	St	MMA	St				
80	20	70.9	29.1	43.33	1.53	55.14	0
60	40	57.8	42.2	21.15	5.54	73.31	3.10
50	50	54.1	45.9	16.04	7.84	76.12	6.67
40	60	49.0	51.0	10.44	12.4	77.16	10.59
20	80	37.1	62.9	3.40	29.2	67.40	20.79

[a] Copolymerization conditions: temp.: 100°C; time: 25 min; concentration of TPSE: $[\text{Monomer}]_0/[\text{TPSE}]_0 = 100 : 1$.

In order to simplify the calculation, in fact, the term of $(I^{1/2}/\delta_1)$ can be regarded as a constant and δ_1/δ_2 might be simply obtained by comparing the polymerization rates of the two monomers alone.[12] The homopolymerization rates of MMA and St using TPSE as initiator can be calculated by the available data in the literature, the R_{MMA} is 4.2×10^{-5} mol ¶ $s^{-1} L^{-1}$ and R_{St} is $1.4 \div 10^{-5}$ mol $\cdot s^{-1} L^{-1}$, respectively. In these conditions, the copolymerization rates (R_p) in different monomer feed ratios can be calculated using following equation:

$$R_p = \frac{-d([M_1] + [M_2])}{dt}/(I^{1/2}/\delta_1)$$

As Table II shows R_p and monomer conversion decreases with the drop of MMA content in feed ratio, which is coincident with the conclusion above mentioned.

Effect of Initiators and Feed Ratio on Sequence Regularity of Copolymer

The thermal properties of poly(St-co-MMA) samples are measured by TGA and DSC. Table III lists the TGA data; here, T_i, T_m, and T_f are the initial decomposition temperature, the decomposition temperature of maximum loss weight, and final decomposition temperature, respectively. It indicates that the samples prepared by the controlled radical method using TPSE as initiator shows a higher thermal stability than the samples obtained by the common radical method using AIBN as initiator. It implies that the copolymer with the higher sequence regularity may be formed in the case of TPSE because the irreversible termination of TMSMD · set the limitation for addition mode of monomer.

Figure 5 shows the DSC results of copolymer samples, which were obtained by several scanning of heating and cooling cycles. The exothermic peaks are observed for TPSE systems, and the more content of St in the feed ratio, the higher the exothermic enthalpy. For the AIBN system, however, in the same conditions no exothermic peaks are found. In order to provide the more reliable expression for this phenomenon, the sequence distribution of the copolymer samples are calculated.[13] As Table IV indicates, the content of successive St sequence in copolymer chain increases with the content of St in feed ratio. For example, if the St content in feed ratio is 20%, the successive St sequence in copolymer is only 1.53%, and no exothermic peak is found; if the St content in feed ratio is 40%, the successive St sequence in copolymer increases to 3.10%, and the corresponding exothermic enthalpy is 3.10 mJ/mg; if the St content increases to 80%, the successive St sequence and the exothermic enthalpy turn to 29.2% and 20.29 mJ/mg, respectively. It is obvious that the crystal melting enthalpy in the DSC diagram is attributed to the PS chain sequence regularity in copolymer, and only for TPSE system can this phenomenon be observed. Thus it can be inferred that in the copolymerization of St and MMA using TPSE as initiator, the copolymer with higher sequence regularity can be obtained, and the more the St content in feed ratio, the higher the sequence regularity of the copolymer.

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