Synthesis of Poly(vinyl acetate)-*graft*-Polystyrene and Application to Preparation of Porous Membranes

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ABSTRACT: Poly(vinyl acetate)–TEMPO (PVAc–TEMPO) macroinitiators were synthesized by bulk polymerization of vinyl acetate in the presence of benzoyl peroxide (BPO) followed by termination with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Radicals were mainly transferred to the acetoxy methyl groups in PVAc during the polymerization. The PVAc–TEMPO macroinitiators had several TEMPO-dormant sites and styrene bulk polymerization with the macroinitiators produced poly(vinyl acetate)-*graft*-polystyrene (PVAc-*g*-PS). All the TEMPO-dormant sites of PVAc–TEMPO macroinitiators participated in the styrene polymerization with almost equal reactivity. Methanolysis of PVAc-*g*-PS broke the PS branches apart from the PVAc backbone chains. Hydrophobic or hydrophilic porous membranes with controlled pore size could be prepared by removing the PVAc domains or the PS domains from the graft copolymer. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1658–1667, 2001

Key words: poly(vinyl acetate); polystyrene; TEMPO; graft copolymerization; porous membrane

INTRODUCTION

Living radical polymerization mediated by TEMPO was initiated by George et al.[1–4] to synthesize polystyrene (PS) with narrow polydispersity. Subsequently, many investigations have been devoted to extending the spectrum of polymerizable monomers, to increase the polymerization rate, and to produce star-shaped polymers,[5] hyperbranched polymers,[6] and random[7] or block copolymers.[8,9]

In this study copolymerization of vinyl acetate and styrene in sequence with TEMPO/BPO was carried out. We were interested in the copolymerization because the copolymer produced would have a better-defined structure compared to that obtained by the conventional graft copolymerization. Because PVAc is immiscible with PS, the copolymer would have a phase-separated morphology, whose domain size depends not only on the copolymer composition but also on the branching architecture of the copolymer.

Vinyl acetate (VAc) was polymerized via a radical mechanism. Many chain-breaking reactions take place during the VAc polymerization as a result of the highly active growing radicals.[10]

Aside from the termination reaction, the chain-transfer reactions, such as the chain transfer to monomer and the chain transfer to polymer, inevitably accompany the VAc polymerization. The acetoxy methyl groups in PVAc have been re-

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Table I Results of Bulk Polymerization of Vinyl Acetate with Benzoyl Peroxide[a]

Sample Code	Polymerization Time (min)	[BPO] M ($\times 10^2$)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	M_w/M_n	Conversion (%)	θ (mol/mol macroinitiator)	θ' [mol/mol of repeating units ($\times 10^{-3}$)]
TP241	60	7.65	87	241	2.77	60	12.9	4.7
TP322	300	1.38	148	322	2.18	27	18.7	5.1
TP210	180	2.06	115	210	1.82	26	16.0	6.7
TP200	140	2.75	110	200	1.80	24	14.9	6.5
TP158	90	3.30	96	158	1.64	13	10.1	5.6
TP136	120	2.06	62	136	2.19	0.01	2.7	1.7

[a] Prepolymerization temperature 60°C; polymerization terminated by 0.064M of TEMPO.

ported to be the principal sites for the chain transfer to polymer reaction. Therefore PVAc moiety could be separated from PS moiety if the two polymer sections were linked via the acetoxy methyl groups because the branches ramifying from the chain transferred acetoxy methyl groups could be alcoholyzed. Porous membranes with a controlled pore size could be prepared by adjusting the copolymer structure and by removing one of the two polymer fractions.

EXPERIMENTAL

Materials

Vinyl acetate (Aldrich, Milwaukee, WI) and styrene (Junsei, Japan) were purified by two courses of vacuum distillation and TEMPO (Aldrich) was used as received. BPO (Acros Organics, NJ) was purified by precipitation from chloroform into methanol and recrystallized in methanol at 0°C.

Instrumentation

Molecular weight and its distribution was measured by GPC [Waters 410, RI detector (Waters Instruments, Rochester, MN), THF eluent, 1.0 mL/min, 30°C, column (porosity: 10 μm, Stragel® HR 1, HR 2, HR 4, Linear)]. Narrow molar mass polystyrene standards (Showadenko SL-105, Japan) were used for the universal calibration.

Graft copolymer was characterized by ^{1}H–NMR spectra recorded at room temperature on a Bruker AC-250 FT-NMR spectrometer (Bruker Instruments, Billerica, MA). A 10-mg sample of

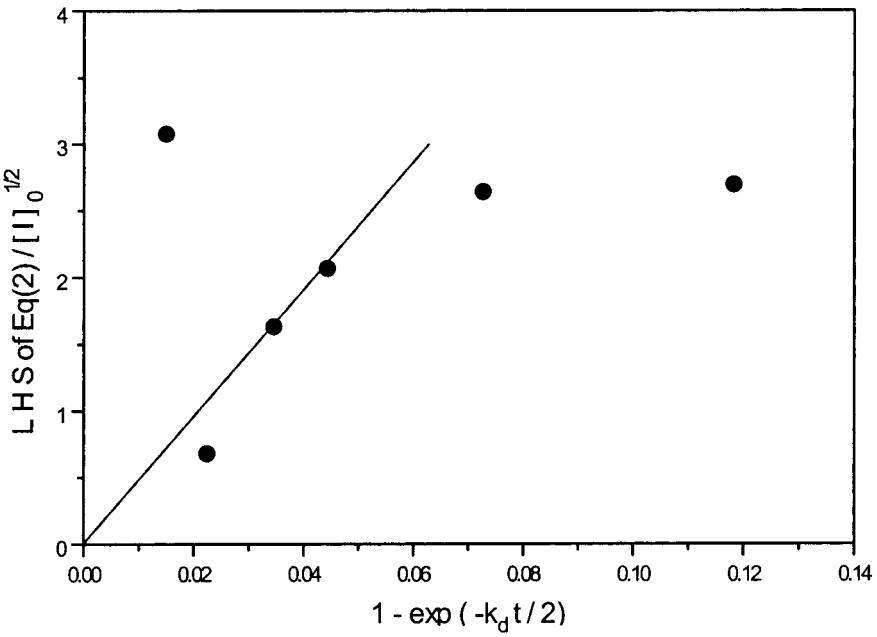


Figure 1 Results of vinyl acetate bulk polymerization.

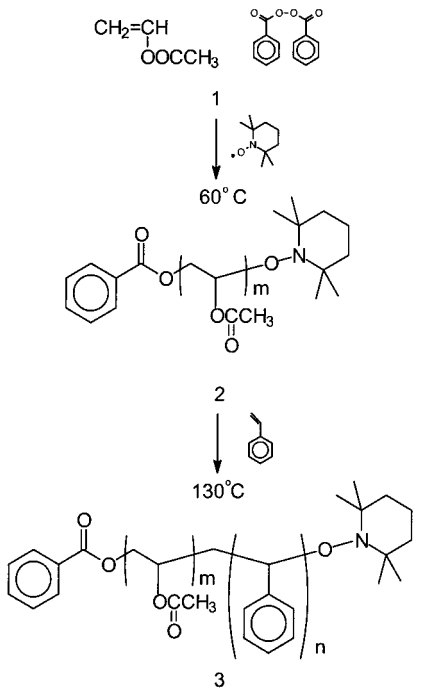


Figure 2 Block copolymerization of TEMPO-terminated PVAc.

the copolymer was dissolved in 0.5 mL of $CDCl_3$ (20 wt/vol %) and was subjected to ^1H–NMR measurements.

PVAc–TEMPO Macroinitiator

Vinyl acetate was bulk-polymerized with different amounts of BPO at 60°C and terminated with an excess quantity of TEMPO. The product was precipitated into *n*-hexane and was Soxhlet-extracted with boiling *n*-hexane for 2 days to remove the unbound TEMPO, and finally dried *in vacuo* to attain constant weight.

PVAc-*g*-PS

PVAc–TEMPO macroinitiator was soluble in styrene, and thus bulk polymerization of styrene in the presence of the macroinitiator at 120°C was easily carried out. The product was precipitated in methanol and dried *in vacuo* followed by Soxhlet extraction with boiling methanol and boiling cyclohexane, in sequence, each for 2 days to remove unreacted PVAc–TEMPO macroinitiators and PS homopolymers formed during the copolymerization.

Porous Membranes

Copolymer films were made by hot pressing at 140°C for 4 min under 4.8 atm, and quickly immersed into ice water. The film thus formed was free from any distortion problems. The film was immersed in 100 mL of 0.5*M* NaOH methanol solution, for 48 h, washed with distilled water, and dried under vacuum, followed by Soxhlet extraction with water for 2 days to remove the unbound PVOH.

The film was fractured while immersed in liquid nitrogen. A scanning electron microscope (Hitachi S-4200, Japan) was used to observe the fractured surface morphology.

RESULTS AND DISCUSSION

Preparation of PVAc–TEMPO Macroinitiators

The kinetics of radical chain polymerization, in general, is expressed as eq. (1):

$$2(1-\sqrt{1-\epsilon x})-\sqrt{1-\epsilon}\left\{\ln\frac{\sqrt{1-\epsilon x}-\sqrt{1-\epsilon}}{1-\sqrt{1-\epsilon}}-\ln\frac{\sqrt{1-\epsilon x}+\sqrt{1-\epsilon}}{1+\sqrt{1-\epsilon}}\right\}=\frac{2k}{k_d}\left\{1-\exp\left(-k_d\frac{t}{2}\right)\right\} \quad (1)$$

where the propagation reaction rate constant (k_p), termination reaction rate catalyst (k_t), initiator efficiency (f), and initiator decomposition rate constant (k_d) are assumed to be constant and k is $k_p(2fk_d)[I]_0/kt$, ϵ is introduced here to take into consideration the density increase of the reaction medium. The value of ϵ is about 0.2 for VAc polymerization and k_d is 8.38×10^{-6} s^{-1} for BPO at 60°C.[10]

With these values, eq. (1) relates the conversion in Table I to polymerization time, as shown in Figure 1, indicating that the kinetics of VAc polymerization cannot be expressed as simply as in eq. (1) because the values of the constants in eq. (1) change greatly with the conversion.

According to Table I, the conversion of TP241, especially, was much higher than that predicted by eq. (1). This is because BPO of high concentration was used and the conversion reached as high as 60% for the preparation of TP241, and the polymerization rate was accelerated as a consequence of the gel or the Trommsdorff effect. Ac-

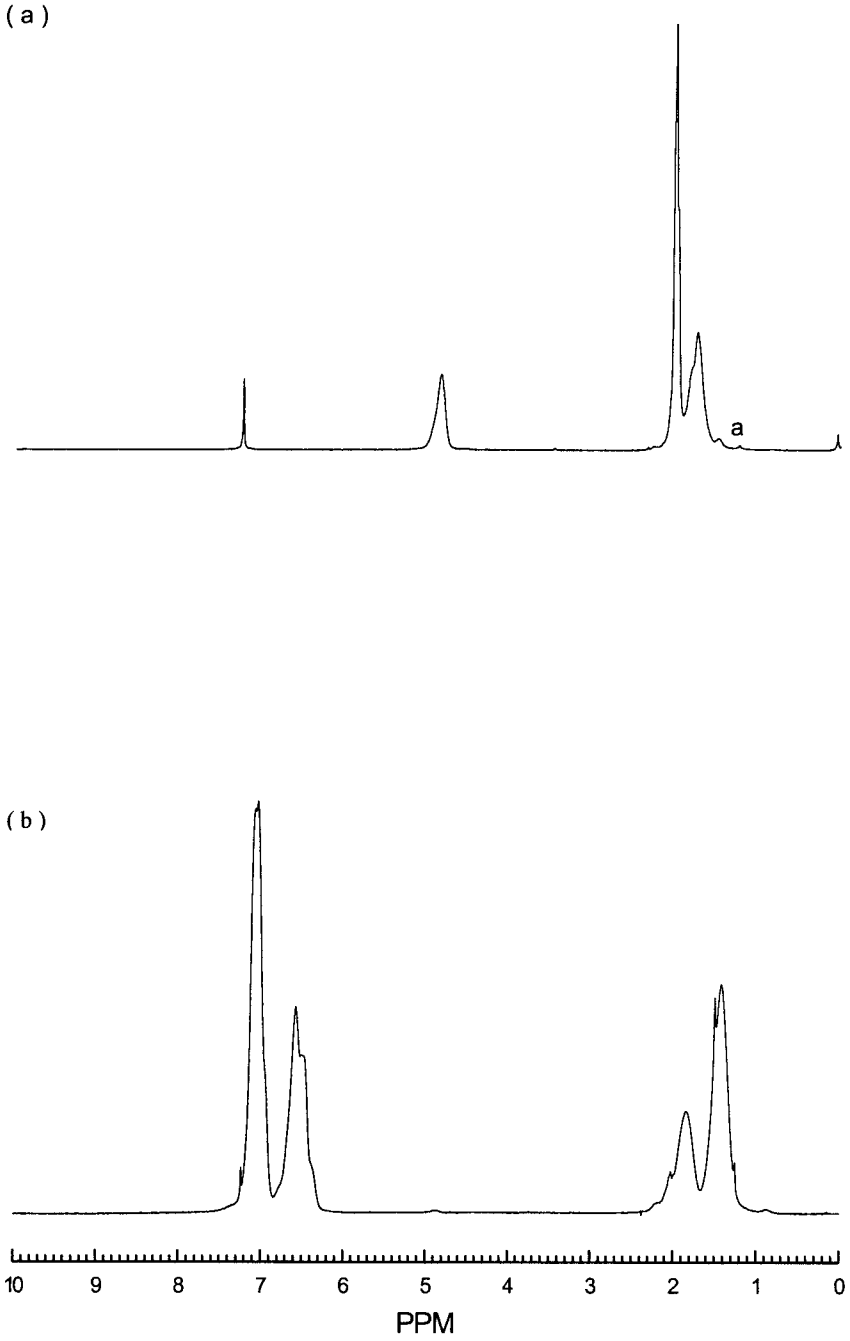


Figure 3 ^{1}H–NMR spectra of (a) TP210 and (b) PS223TP210.

tually, TP241 contained 12.5 wt % of insoluble fraction in methanol, whereas TP210, TP200, and TP158 were dissolved completely in methanol.

The theoretical value of the polydispersity (M_w/M_n) is 2.0 for polymers when the chain transfer and the disproportionation termination are the principal dominating chain-breaking reactions. Table I illustrates that the polydispersity of the sol fraction in TP241 was as broad as 2.77, whereas the other PVAc–TEMPO macroinitiators had polydispersity in the range between 1.64 and 2.19. The gelation takes place as a result of the chain transfer to polymer reactions, and therefore PVAc–TEMPO macro-

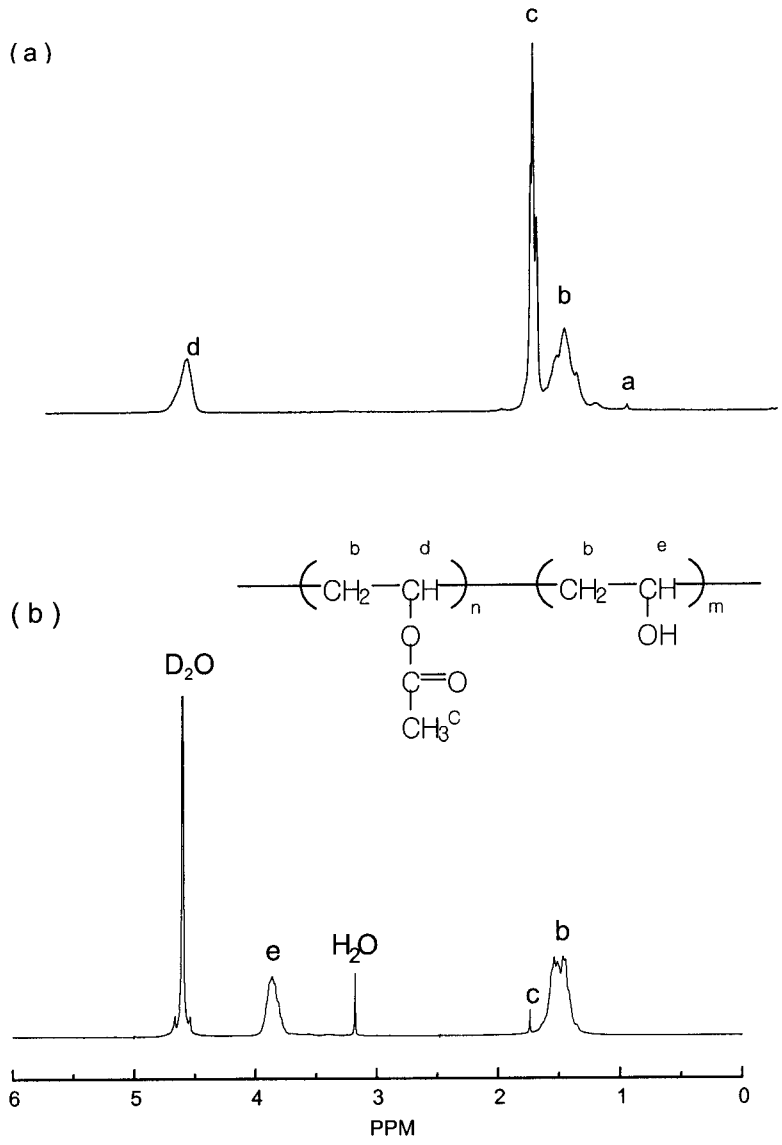


Figure 4 ^{1}H–NMR spectra of TP210 before (a) and after (b) methanolysis.

initiators could have a different number of TEMPO molecules in their chain, depending on the ratio of the radical transfer rate to the radical elimination rate (see Fig. 2).

Figure 3(a) shows ^{1}H–NMR spectra of PVAc–TEMPO. The tetramethyl protons of TEMPO exhibit their peak at 0.8–0.9 ppm. The number of TEMPO molecules per VAc unit, θ', can be calculated using eq. (2):

$$\frac{12\theta'}{6 + 11\theta' + 12\theta'} = \frac{\text{Area of peak at 0.8–0.9 ppm}}{\text{Total peak area}} \quad (2)$$

Weight-average molecular weight (M_w) is expressed in terms of θ' and weight-average degree of polymerization (DP) in eq. (3):

$$M_w = 86\left(\text{DP} - \frac{\theta'}{1 + \theta'}\,\text{DP}\right) + 241\,\frac{\theta'}{1 + \theta'}\,\text{DP} \quad (3)$$

where the θ'[DP/(1 + θ')] term corresponds to the number of TEMPO molecules per macroinitiator molecule (θ). In a radical chain polymerization system, growing polymer radicals coexist with dead polymer molecules, and the concentration of

Table II Characteristics of PVAc-*graft*-PS[a]

A

	MeOH Soxhlet-Extracted Fraction		Residual Fraction After MeOH Soxhlet Extraction	
Sample Code	Wt % Extracted	VAc Unit Molar Content (%)	Wt % Remaining	VAc Unit Molar Content (%)
PS285TP210	1.7	96.2	98.3	15.6
PS402TP200	1.0	100.0	99.0	11.4
PS349TP158	2.3	100.0	97.7	9.8
PS551TP241	1.7	96.0	98.3	11.0

B

	Cyclohexane Soxhlet Extracted Fraction		Residual Fraction After Cyclohexane Soxhlet	
Sample Code	Wt % Extracted	VAc Unit Molar Content (%)	Wt % Remaining	VAc Unit Molar Content (%)
PS285TP210	26.9	4.4	73.1	18.8
PS402TP200	20.0	10.9	80.0	14.2
PS349TP158	21.2	5.5	78.7	13.3
PS551TP241	21.6	5.5	78.4	12.1

C

	Macroinitiator		Copolymer		
Sample Code	M_n ($\times 10^{-3}$)[b]	M_w ($\times 10^{-3}$)[b]	M_n ($\times 10^{-3}$)[b]	M_w ($\times 10^{-3}$)[b]	M_w ($\times 10^{-3}$)[c]
PS285TP210	115	210	170	285	1307
PS402TP200	110	200	161	402	1662
PS349TP158	96	158	181	349	1403
PS551TP241	89	278	273	551	2358

[a] Copolymerization time, 20 h; copolymerization temperature, 120°C.
[b] Measured by GPC.
[c] Estimated from M_w of the macroinitiator and the copolymer composition.

the former is generally much lower than that of the latter. Therefore the radical transfer takes place mostly onto the dead polymer molecules and it is hardly probable that a growing polymer would have more than two radicals at the same time.

However, Table I shows that the values of θ are much greater than those expected. The value of θ was 2.7 mol/mol of macroinitiator, even when the conversion was as low as 0.01, which was far below the gel point (TP136), and the value of θ increased as the conversion increased. The θ value of TP241 was lower compared to that of the other macroinitiators because radicals on the growing polymer molecules (at a conversion as high as 60%) were terminated either by crosslinking or by other termination reactions.

Preparation of PVAc-*g*-PS

Radical chain transfer to PVAc occurs mainly on site (C) rather than on site (B),[11] as shown in the following schematic:

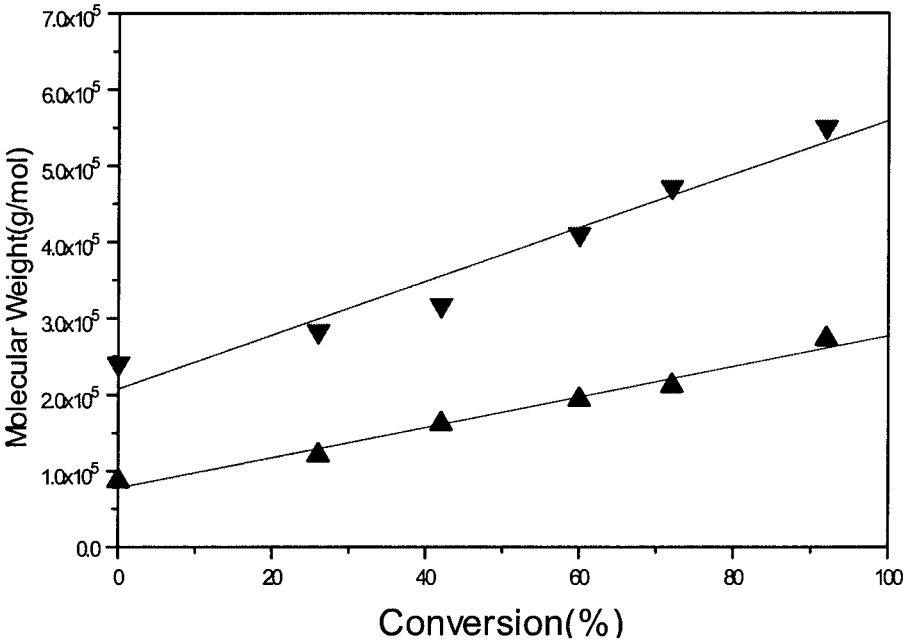
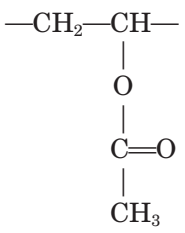


Figure 5 Molecular weight as a function of conversion for bulk polymerization of styrene using the macroinitiator TP241. Polymerization temperature, 120°C; ▲, M_n; ▼, M_w.

(A) (B)



(C)

When TEMPO molecules are bonded to (C), they would hydrolyze easily. TP210, whose ^{1}H–NMR spectrum is shown in Figure 4, was hydrolyzed in KOH methanol solution for 24 h. The ^{1}H–NMR spectrum of the resulting product is shown in Figure 4(b). The peak at 0.8 ppm in Figure 4(a) disappeared from Figure 4(b), demonstrating that TEMPO molecules bonded to the acetoxy methyl groups were removed during the alcoholysis procedure.

Styrene was bulk-polymerized with the PVAc–TEMPO macroinitiators, the results of which are shown in Table II. As stated earlier, once macroinitiator molecules had several TEMPO-bonded dormant sites, the resulting copolymer should be PVAc-*g*-PS with PVAc backbone chain carrying several PS branches.

Products from the copolymerization were Soxhlet-extracted with boiling methanol to separate PVAc homopolymer. The amount of the Soxhlet-extracted fraction was 1.0–2.3% (Table IIA), indicating that almost all the PVAc molecules participated in the copolymerization with styrene. These results confirm the previous conclusion in that few PVAc molecules were devoid of active radicals on them, at least near the conversion where the gel effect came into effect. The residual fraction after the methanol Soxlet extraction was subjected to cyclohexane Soxhlet extraction to remove the PS homopolymer by-product. However, the amount of VAc units contained in the cyclohexane Soxhlet-extracted fraction could certainly not be considered negligible (Table IIB). Table IIC summarizes average molecular weight of PVAc-*g*-PS after the two-step Soxhlet extraction measured by GPC. In the last column of Table IIC, weight-average molecular weight (M_w) estimated using the data of M_w of PVAc–TEMPO and the composition of PVAc-*g*-PS from the ^{1}H–NMR spectra.

Number-average and weight-average molecular weights (M_n and M_w) of the copolymer measured by GPC increased linearly with the conversion, as shown in Figure 5. However, M_w from the GPC measurements was much lower than that

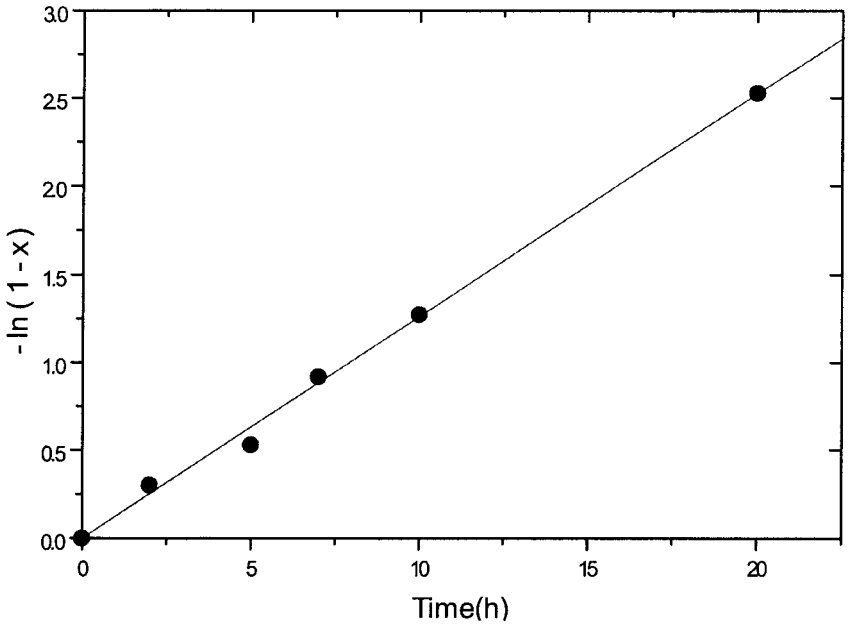


Figure 6 Semilogarithmic plot of M_0/M_t as a function of polymerization time for bulk polymerization of styrene using TP241. Polymerization temperature, 120°C.

estimated from the copolymer composition. This was attributed to the fact that the hydrodynamic volume of PVAc-*g*-PS in the GPC measurement did not increase linearly with the real molecular weight because of the branched structure of the copolymers.

Contrary to expectations, the content of styrene units was higher in PVAc-*g*-PS made from PVAc–TEMPO macroinitiator with a smaller value of θ, which seemed to be attributed to the fact that the copolymer molecules rich in styrene units were removed during the cyclohexane

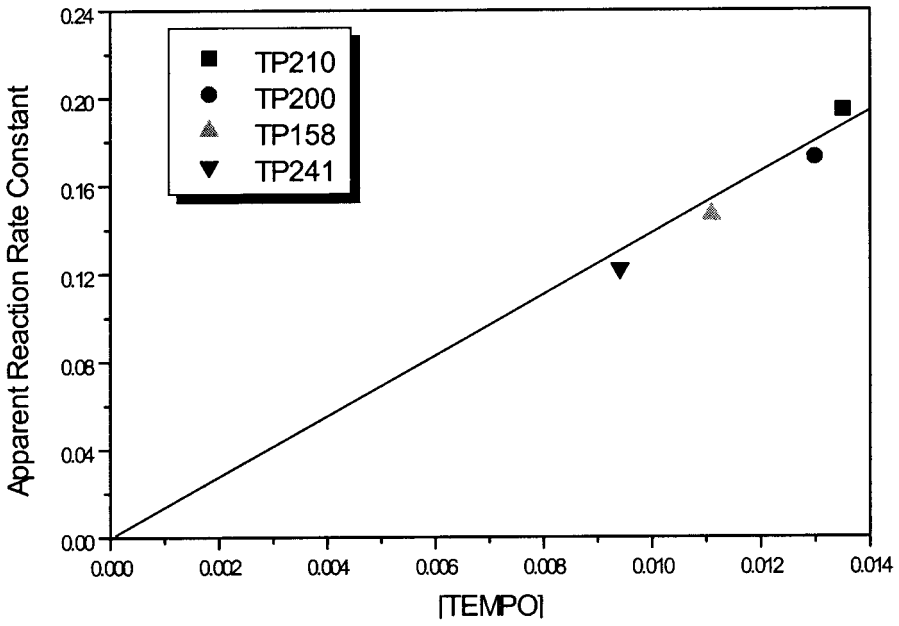
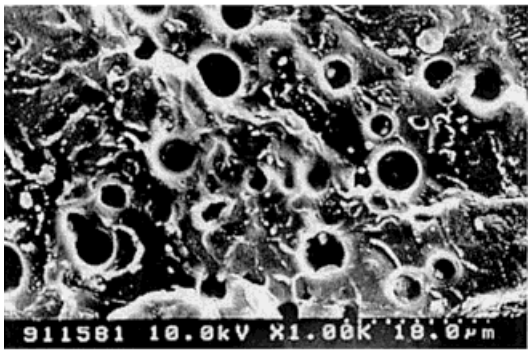
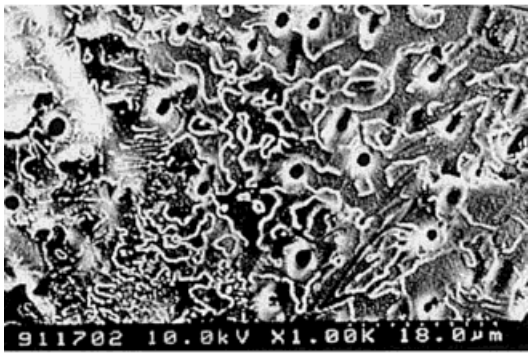


Figure 7 Effect of macroinitiator concentration on the rate of styrene bulk polymerization.

(a)



(b)



(c)

Figure 8 Scanning electron photomicrographs of fractured surface of PS223TP210 film (a) after methanolysis and (b) after Soxhlet extraction; (c) fractured surface of PS286TP158 film after Soxhlet extraction.

Soxhlet extraction. Figure 6 illustrates that bulk polymerization of styrene using the PVAc–TEMPO macroinitiator can be represented by the first-order reaction rate constant. Figure 7 shows that the apparent reaction rate constant is a linear function of TEMPO concentration in the macroinitiator, confirming that all the TEMPO dormant sites participated in the styrene bulk polymerization with equal reactivity.

Preparation of Porous Membranes

The PVAc is converted into poly(vinyl alcohol) (PVA) by the hydrolysis of the copolymer with KOH methanol solution, and the PVAc moiety is to be cleaved away from the PS part because PS branches in PVAc-*g*-PS are bonded mainly to the acetoxy methyl groups of PVAc. Soxhlet extraction of the resulting copolymer sheet with water below the glass-transition temperature of PS would dissolve out the PVA moiety, leaving pores behind, whereas the PS matrix remains intact.

Figure 8 shows a fractured surface of PS285TP210 sheet (VAc unit content, 18.8 mol %) after methanolysis [Fig. 8(a)] and after water Soxhlet extraction [Fig. 8(b)]. Pores of 2–5 μm were created in the Soxhlet-extracted PS285TP210 sheet. The same experiment was carried out using PS349TP158 (VAc unit content, 13.3 mol %), and the resulting sheet had pores of 1–2 μm, indicating that the size of the pores was largely determined by the copolymer composition. PVAc-*g*-PS had a phase-separated morphology, and the domain size of each phase should be much smaller than that of each phase in a simple PVAc/PS blend.

The pore size of polymer membranes made from polymer blends can be controlled thermodynamically by the compatibility between the polymer components. A more compatible polymer blend system yields membranes with smaller pore size. However, in this case, the solvent becomes quite limited in its ability to selectively remove one of the polymer components.

CONCLUSION

This study suggests a possibility for preparation of hydrophobic PS membrane or hydrophilic PVA membrane with controllable pore size by adjusting molecular weight, composition, or degree of branching from PVAc-*g*-PS copolymer.

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