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Polymerization Behavior of Novel Vinyl Monomers Containing Pyrrolidone Moieties

Ichiro Atobe, Toshikazu Takata, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

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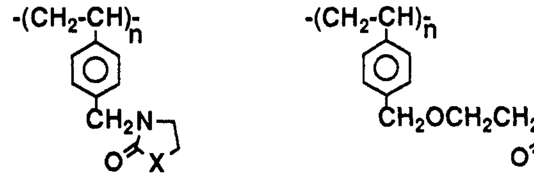
ABSTRACT: Homopolymerization of novel pyrrolidone-containing vinyl monomers, 4-[(2-oxo-1-pyrrolidinyl)methyl]styrene (PS) and 4-[[2-(2-oxo-1-pyrrolidinyl)ethoxy]methyl]styrene (PES), and their copolymerizations with styrene (St), *p*-methoxystyrene (PMS), and *m*-hydroxystyrene (MHS) were investigated. The polymerization behavior of PS and PES [P(E)S] was compared with that of oxazolidone-containing vinyl monomers. Polymerization of PS at a high monomer concentration gave gelled polymer, while in the polymerization of PES soluble polymer was obtained without any gelled polymer even in bulk condition. Copolymerizations of P(E)S with styrene derivatives were carried out to estimate copolymerization parameters which were obtained by both nonlinear least-squares (NLLS) and Fineman–Ross methods (FR). The alternating copolymerizability decreased in the order St > PMS > MHS, which was suggested to result from the difference in strength of the interaction between pyrrolidone moieties and aromatic groups of styrene derivatives. The copolymerization behavior of P(E)S with MHS was compared with that of 4-[(2-oxo-3-oxazolidinyl)methyl]styrene (OS) and 4-[[2-(2-oxo-3-oxazolidinyl)ethoxy]methyl]styrene (OES). The alternating copolymerizability of P(E)S with MHS was superior to that of O(E)S with MHS. From the spectroscopic study such as ^{1}H NMR and IR, the difference of the copolymerization behavior was dependent on the interaction between P(E)S-MHS and O(E)S-MHS. It was suggested that the interaction between the oxazolidone moiety and phenolic group is attributed only to hydrogen bonding while that between the pyrrolidone moiety and phenolic group comes from the both hydrogen bonding and C–T stacking.

Introduction

It is well-known that polymers having a pyrrolidone or oxazolidone moiety are useful as complexing agents for phenols, alkyl halides, halogens, and metal ions.[1–8] We have already reported the complex formation of phenols with bifunctional pyrrolidones as model compounds of the polymers.[9] It was suggested that strength of the interaction between the pyrrolidone moiety and phenolic group decreases with increase of the distance between polymer main chain and the pyrrolidone moiety.[9] Therefore, we have designed vinyl monomers containing a spacer between the vinyl group and the pyrrolidone or oxazolidone moiety, such as PS, PES, OS, and OES as shown below.[10,11]



X: CH_2 (PS) X: CH_2 (PES)
O (OS) O (OES)

Meanwhile, in the copolymerization of PS and PES (both PS and PES are abbreviated as P(E)S) or OS and OES (both OS and OES are abbreviated as O(E)S) with some comonomers which are able to interact with those monomers, it is expected that the copolymer obtained would have some alternating structure. In our previous paper,[10] we have reported that the copolymerization of O(E)S with *m*-hydroxystyrene (MHS) shows a weak alternating copolymerizability. The present paper deals with homopolymerization of P(E)S and copolymerization of P(E)S with styrene (St), *p*-methoxystyrene (PMS), and *m*-hydroxystyrene (MHS) and comparison of the polymerization behavior with that of O(E)S.

Experimental Section

Materials. 4-[(2-Oxo-1-pyrrolidinyl)methyl]styrene (PS), 4-[[2-(2-oxo-1-pyrrolidinyl)ethoxy]methyl]styrene (PES), and *m*-hydroxystyrene (MHS) were synthesized according to the previously reported method.[11] Vinylpyrrolidone (VP, Wako Pure Chemical Industries Inc.) was purified by distillation *in vacuo* (bp 62–63 °C/2 mmHg) after dehydration with calcium hydride. Other chemicals and solvents were purified according to common procedures.

Homopolymerization. General Procedure. Homopolymerization of PS and PES was carried out at 60 °C for 24 h in a sealed tube in bulk or in dry benzene under the conditions of various monomer concentrations, using azobisisobutyronitrile (AIBN 1 mol %). The polymer obtained was precipitated with *n*-hexane and dried under reduced pressure.

Time-Conversion Curve of Polymerization. A mixture of PS or PES and AIBN (1 mol %) in benzene-d_6 (14 equiv) in a sealed NMR tube was heated at 60 °C in an oil bath. At intervals, the tube was taken out and its ^{1}H-NMR spectrum was measured to estimate the consumption of the monomer. The polymerizations of *N*-vinylpyrrolidone (VP) and St, as reference monomers, were similarly carried out.

Copolymerization of PS and PES with Styrene Derivatives. General Procedure. A mixture of PS or PES and a styrene derivative in dry benzene [for P(E)S–St, P(E)S–PMS], acetonitrile [for P(E)S–MHS], or dimethyl sulfoxide (for PS–MHS) (total concentration = 2.5–3.5 mol dm^{-3}) was placed in an ample tube containing a small stirred tip and AIBN (1 mol %). The tube was evacuated and sealed off. The mixture was heated at 60 °C for 30–60 min. The product was directly poured into hexane (for P(E)S–St, P(E)S–PMS) or nitromethane–either mixed solvent [for P(E)S–MHS] to precipitate the corresponding copolymer which was collected by decantation and dried in vacuo. Copolymer composition was determined by elemental analysis (N content of the copolymer).

Measurement. ^{1}H NMR spectra were recorded on a JNM PMX-60si NMR spectrometer (60 MHz) using tetramethylsilane as an internal standard. FT-IR spectra were measured with a JASCO FT-IR/3 spectrometer. Number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) were determined with a TOSOH HLC-8020 GPC system (polystyrene gel; eluent: DMF containing 0.003 mol/L of lithium bromide; flow rate 1.0 mL/min).

Measurement of IR Spectrum. P(E)S or OS was mixed with phenol, *m*-hydroxystyrene (MHS), or *p*-*tert*-butylphenol in molar ratios ranging from 0 to 8 ((MHS/P(E)S or O(E)S) in

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Table I. Homopolymerization of PS and PES[a]

			polymer			
			yield (%)			
run	monomer	solvent	insoluble	soluble	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$
1	PS	none	29[c]	65[c]	200 000	3.05
2	PS	benzene (100 mol %)	12[c]	83[c]	205 000	3.41
3	PS	benzene (300 mol %)		100[d]	189 000	2.99
4	PES	none		100[d]	91 000	3.61
5	PES	benzene (100 mol %)		97[c]	86 000	3.12

[a] Polymerization was performed in benzene or in bulk at 60 °C using AIBN (1 mol %). [b] Estimated by GPC (based on PSt). [c] Precipitated in n-hexane, after extracted by the Soxhlet extractor with $CHCl_3$. [d] Precipitated in n-hexane.

dry acetonitrile ([C] = 2.0–2.5 mol dm^{-3}) or without solvent. In the absence of solvent, the mixture was fused by heating at 50 °C for 5 min in an oil bath, and then a portion of the mixture was subjected to the IR measurement (neat). When the solvent was used, after the mixture was stirred at 25 °C for 5 min the IR spectrum of a portion of the mixture was recorded (neat). The carbonyl adsorption band of the pyrrolidone or oxazolidone group was determined from the spectrum in an error of wavenumber within 2 cm^{-1}.

Measurement of ^{1}H NMR Spectrum. PS or OS was mixed with one of the styrene derivatives in molar ratios ranging from 1 to 8 (phenols/PS or OS) without solvent. The mixture was fused by heating at 50 °C for 5-min in an oil bath. The ^{1}H NMR spectrum of the resulting mixture was measured at a concentration of [C] = 0.5 mol dm^{-3} in benzene-d_6 (PS or OS–St, PS or OS–PMS) or acetonitrile-d_3 (PS or OS–MHS). The chemical shift was determined within an error of 0.02 ppm.

Results and Discussion

Homopolymerization. Radical polymerizations of PS and PES were carried out at 60 °C for 24 h in bulk or in dry benzene in various monomer concentrations, using AIBN as an initiator. These results are summarized in Table I. PS and PES quantitatively polymerized under the conditions. In the polymerization of PS at high monomer concentration, gelled polymer was formed, while no such gelled polymer was obtained in the case of PES even in bulk polymerization. In the polymerization of PS, more than 300 mol % of benzene as solvent was needed to suppress the formation of the gelled polymer. Although the exact mechanism is not clear, the formation of the gelled polymer from PS seems to occur by reaction of benzyl radical formed by the abstraction of benzyl hydrogen of PS during the polymerization, judging from the ease of the hydrogen abstraction and the concentration dependent gelation. Poly(PS) obtained was a white powder, while poly(PES) was a yellow transparent gummy solid.

Rates of the polymerizations of PS and PES were estimated by time–conversion curves and compared with those of styrene (St) and vinylpyrrolidone (VP). The polymerization was carried out at 60 °C in benzene-d_6 using AIBN (1 mol %) as an initator in a sealed NMR tube. Time-conversion curves of these monomers are shown in Figure 1. The polymerization rate of these monomers decreases in the following order: VP (kp = 953 L/mol s at 20 °C[12]) > PS > PES > St (kp = 24 L/mol s at 20 °C[13]). This result suggests that *para* substituents containing these pyrrolidone moieties serve as an electron-withdrawing group, whereas PS and PES can be regarded as styrene derivatives. Electron-withdrawing substituents of styrene derivatives accelerate the radical polymerization.[14] Under the conditions, VP polymerized fastest of all and ca. 2.5 times faster than PS or PES. The polymerization of PES was slightly slower than that of PS but 1.5–2 times faster than that of St.

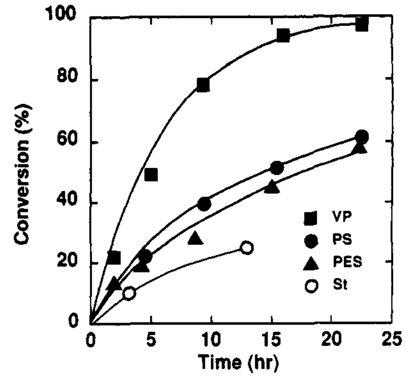

Figure 1. Time–conversion curves of radical polymerization of PS, PES, St, and VP with AIBN (1 mol %) in benzene-d_6 (14 equiv) at 60 °C.

Table II. Copolymerization Parameters of PS and PES in the Copolymerization with Styrene Derivatives

monomer					
M_1	M_2	r_1	r_2	r_1r_2	calcn method
PS	St	0.856	1.014	0.868[a]	NLLS[d]
		0.839 ± 0.003	0.995 ± 0.001	0.835[a]	FR[e]
PS	PMS	0.732	0.782	0.572[a]	NLLS[d]
		0.707 ± 0.009	0.772 ± 0.004	0.546[a]	FR[e]
PS	MHS	0.231	0.708	0.164[b]	NLLS[d]
		0.204 ± 0.029	0.654 ± 0.006	0.133[b]	FR[e]
PS	MHS	0.529	1.514	0.801[c]	NLLS[d]
		0.412 ± 0.052	1.306 ± 0.012	0.538[c]	FR[e]
OS	MHS	0.501	0.560	0.281[b,f]	NLLS[d]
		0.483 ± 0.104	0.559 ± 0.032	0.270[b,f]	FR[e]
PES	St	0.949	0.974	0.924[a]	NLLS[d]
		0.909 ± 0.025	0.934 ± 0.011	0.849[a]	FR[e]
PES	PMS	0.890	0.940	0.837[a]	NLLS[d]
		0.748 ± 0.061	0.787 ± 0.024	0.589[a]	FR[e]
PES	MHS	0.549	0.883	0.485[b]	NLLS[d]
		0.544 ± 0.006	0.859 ± 0.002	0.467[b]	FR[e]
OES	MHS	0.593	0.623	0.369[b]	NLLS[d]
		0.694 ± 0.122	0.732 ± 0.046	0.508[b]	FR[e]

[a] In benzene. [b] In acetonitrile. [c] In dimethyl sulfoxide. [d] Nonlinear least-squares analysis. [e] Fineman–Ross method. [f] Reference 10.

Copolymerization with Styrene Derivatives. Copolymerizations of PS and PES (M_1) with St, PMS, and MHS (M_2) were carried out in dry benzene, acetonitrile (for MHS), or dimethyl sulfoxide (for MHS) using AIBN (1 mol %) as an initiator at 60 °C for 30–60 min. Conversion of the monomers was kept at ca. 5% to facilitate easy determination of copolymerization parameters (r_1, r_2). Compositions of the obtained copolymers were estimated by their elemental analysis data (N content in the copolymers). The copolymerization parameters were calculated by both the nonlinear least-squares analysis method (NLLS)[15] and the Fineman–Ross method (FR). Results are summarized in Table II. The copolymerization parameters calculated by these two methods were fairly close as shown in Table II. The copolymerization behavior of PS and PES was evaluated using the parameters calculated by the NLLS method. Alfrey–Price Q–e values of PS and PES calculated from the r_1, r_2 values are listed in Table III. Feed ratio–copolymer composition curves were obtained from either the compositions of the copolymers (plots, ●, ▲) and the copolymerization parameters of Table II (- - -), as shown in Figures 2 and 3.

The r_1r_2 values of the copolymerizations with the styrene derivatives were lowered in the order St > PMS > MHS in the cases of PS and PES. The copolymer composition curve of PS and St demonstrates the occurrence of

Table III. *Q* and *e* Values of PS, PES and Related Monomers

monomer	Q	e	method
PS	0.730	–0.424[a]	NLLS[e]
	0.715	–0.375[a]	FR[f]
	0.529	0.546[b]	NLLS[e]
	0.540	0.619[b]	FR[f]
PES	0.820	–0.519[a]	NLLS[e]
	0.775	–0.395[a]	FR[f]
	0.631	0.051[b]	NLLS[e]
	0.637	0.072[b]	FR[f]
St	1.0	–0.8[c]	
PMS	1.36	–1.11[d]	
MHS	1.10	–0.8[d]	

[a] Based on St in benzene. [b] Based on MHS in acetonitrile. [c] Reference 16. [d] Reference 17. [e] Obtained from the reactivity ratios by calculation with the nonlinear least-squares method. [f] Obtained from the reactivity ratios by calculation with the Fineman–Ross method.

approximately random copolymerization ($r_1r_2 = 0.868$), while that of PS and PMS denotes a little alternating copolymerizability ($r_1r_2 = 0.572$). In the case of PS and MHS a somewhat clear alternating copolymerizability ($r_1r_2 = 0.164$) can be confirmed (Figure 2).

On the other hand, Q and e values of St (1.0, –0.8) are nearly equal to those of MHS (1.10, –0.8) as shown in Table III. The Q and e values of PS obtained with St were 0.73 and –0.42, respectively, while those of PS obtained with MHS were 0.53 and +0.55, respectively. In addition, the copolymer composition curves of PS–PMS and PS–MHS obtained experimentally from the composition of the copolymers were significantly different from those drawn from the copolymerization parameters (Figure 2b,c). Similar results to those with PS mentioned above were obtained with PES. These differences in the Q–e values and the composition curves might be explained by assuming the influence of a particular intermolecular interaction which arises during the copolymerization. Complex formation between pyrrolidonyl and phenolic groups contained within individual monomers concerned with the copolymerization, respectively, would strongly affect the copolymerization. The interaction can be seen between monomer–comonomer, polymer–(co)monomer, and/or polymer–polymer, if solvent is not taken into consideration. Namely, judging from the papers[6–8] reported so far, in the copolymerization of PS and MHS, the interaction between the pyrrolidone moiety of PS and the phenol group of MHS is caused probably in terms of both hydrogen bonding (between the amide group of PS and the phenolic hydroxy group of MHS) and C–T stacking (between the two groups in which electron-donation from benzene ring of MHS to amide moiety of PS takes place). Since there is no interaction due to hydrogen bonding in the copolymerization of PS with PMS, the interaction between the two groups should be weak, as expected from the much reduced alternation between them observed above. Presumably, little C–T interaction occurs.

If the interaction between the pyrrolidone and the phenol groups occurs by the two factors mentioned above, it should be disturbed by an additive having a large donation number such as dimethyl sulfoxide (DMSO). The effect of such an additive might be larger than that of one with a high polarity such as acetonitrile, which could be used as the solvent for the copolymerization with MHS. In fact, the r_1r_2 value of the copolymerization of PS with MHS in DMSO as solvent was 0.801 which was much larger than that obtained in acetonitrile (0.164, as shown in Table II, and accordingly the copolymer composition curve (▲) was significantly different (Figure 2c). This result suggests that DMSO sharply suppresses the interaction between the two groups, lowering the alternating copolymerizability, perhaps by disturbing not only hydrogen bonding but also C–T interaction.

PS showed the higher alternating copolymerizability with the styrene derivatives than PES with the styrene derivatives. This difference would be attributed to the different spacer length. PES has the longer and more flexible spacer than PS. If the strength of the interaction of the two groups capable of interacting with one other is similar in PS and PES, the shorter spacer length between the reaction centers could lead to more efficient alternating copolymerization.

In the previous paper,[10] we have studied the copolymerization behavior of oxazolidone group-containing vinyl monomers (OS and OES) with the same styrene derivatives. The results obtained with PS and PES in this paper are similar to those obtained with respect to OS and OES from the viewpoint of effects of the length of the spacer and the substituent in the styrene derivative. Thus, OS has alternating copolymerizability greater than OES, and MHS shows the smallest r_1r_2 value among the three styrene derivatives in the case of either OS and OES. Comparison of the r_1r_2 values indicates more efficient alternating copolymerization of P(E)S than O(E)S (PS–MHS, $r_1r_2 = 0.164$; OS–MHS, $r_1r_2 = 0.281$). This suggests that the interaction of pyrrolidone group with phenol group is stronger than that of oxazolidone group. The difference in strength of the interaction between P(E)S and O(E)S is described later.

Monomer–Comonomer Interaction. Interaction between monomers in the copolymerization of PMS or MHS with P(E)S appears to be one of the important factors influencing alternating copolymerizability. To estimate this interaction, the following spectroscopic experiments were examined.

In IR work, shift of carbonyl absorption of P(E)S by addition of MHS was measured in molar ratios of MHS/P(E)S ranging from 0 to 8 in dry acetonitrile ([C] = 2.5–3.0 mol dm^{-3}). Results are shown in Figure 4. A considerable shift of the carbonyl absorption of P(E)S to lower frequencies was observed. The degree of the shift to lower frequencies increased according to the increase of the amount of MHS added. The maximum shift was ca. 40 cm^{-1} which was observed by the addition of 8 equiv of MHS. Occurrence of this carbonyl shift is consistent with our previous reports on the IR work describing the interaction between bifunctional pyrrolidone and phenols.[9] The maximum shift value (ca. 40 cm^{-1}) of P(E)S which is larger than that of O(E)S (ca. 30 cm^{-1})[10] seems to correspond to the alternating copolymerizability higher than that of O(E)S.

In ^{1}H NMR study on the change of chemical shift of each signal of PS by addition of the styrene derivatives (Figure 5), methylene signals a and b were confirmed to be shifted to lower field by the addition of MHS (PS–MHS). The higher field shift observed is probably attributed to the ring current effect of the benzene ring of MHS which would be connected by C–T interaction with the amide group. Meanwhile, the lower field shift can be accounted for by assuming a decrease of electron density around the amide carbonyl by hydrogen bonding. The results of PS–MHS agree with those PS–St and PS–PMS in which no lower field shift of proton signal was observed, due to the absence of hydrogen bonding. Further, the higher field shift presumably due to C–T stacking is observed in PS–St and PS–PMS systems. The change of the chemical shifts in PS–PMS systems is slightly

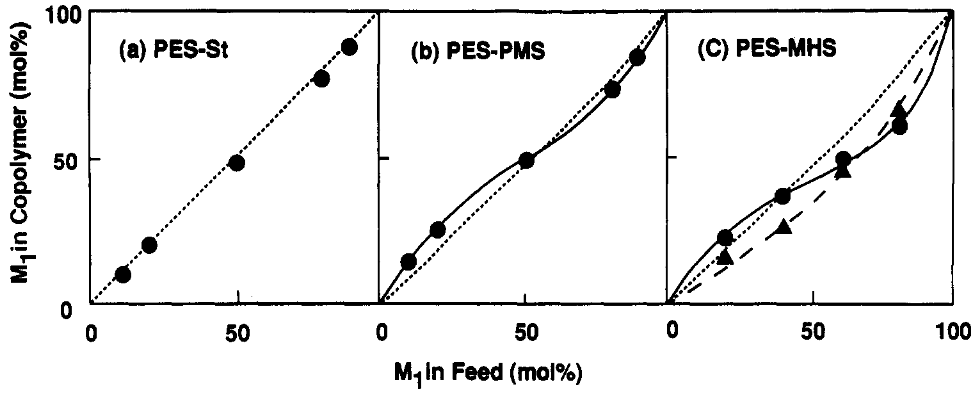

Figure 2. Copolymer composition curves of copolymerizations of PS (M_1) with St, PMS, and MHS: - - -, calculated curve using the copolymerization parameters; ● [in benzene (PS–St or PMS) or acetonitrile (PS–MHS)] or ▲ [in dimethyl sulfoxide (PS–MHS)]; plots of the composition of the copolymers.

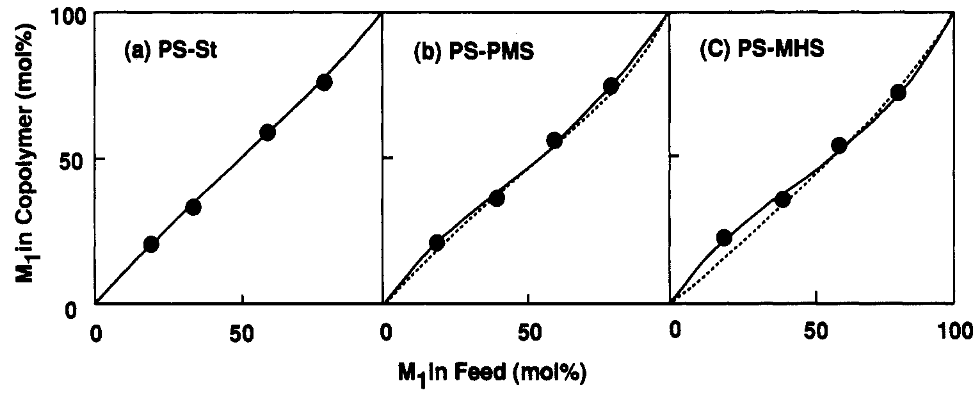

Figure 3. Copolymer composition curves of copolymerizations of PES (M_1) with St, PMS, and MHS: - - -, calculated curve using the copolymerization parameters; ●, plots of the compositions of the copolymers.

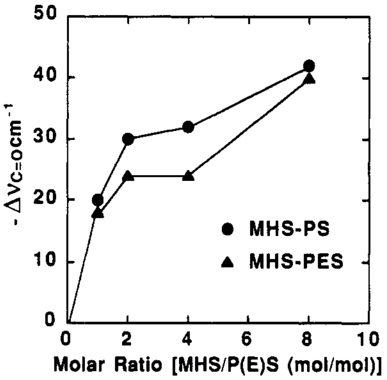

Figure 4. Change of IR carbonyl adsorption ($\nu_{C=O}$) of PS and PES by addition of MHS in acetonitrile ([C] = 2.5–3.0 mol dm^{-3}) at 25 °C.

larger than that of St, since the methoxy group of PMS can serve as an electron-donating group.

In the previous discussion the authors pointed out the difference in alternating copolymerizability of P(E)S and O(E)S. Both hydrogen bonding and C–T stacking were operative in the P(E)S–MHS systems. Formation of hydrogen bonding was confirmed in the system of O(E)S–MHS in our previous study.[10] Therefore, the authors examined the possibility of C–T stacking in the system of OS-MHS to clarify the difference. As shown in Figure 6, there was no significant change in chemical shift of methylene signals a and b of OS by addition of styrene derivatives in ^{1}H NMR study in benzene-d_6 or acetonitrile-d_3. In comparison with the results of Figure 5, this result seems to suggest the absence of the C–T stacking between oxazolidone and phenol groups. Thus, the difference between P(E)S and O(E)S is strongly suggestive of C–T stacking. Although the reason why C–T stacking is absent

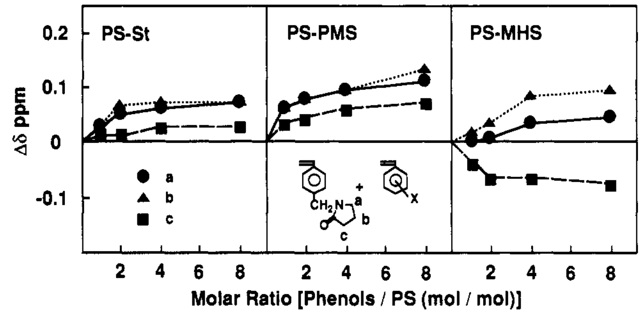

Figure 5. Change of ^{1}H-NMR chemical shift of PS by addition of styrene derivatives in benzene-d_6 (PS or OS–St, PS or OS–PMS) or acetonitrile-d_3 (PS or OS–MHS) ([C] = 0.5 mol/L).

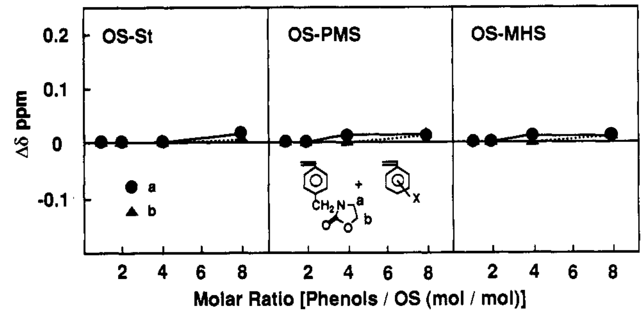

Figure 6. Change of ^{1}H-NMR chemical shift of OS by addition of styrene derivatives in benzene-d_6 (PS or OS–St, PS or OS–PMS) or acetonitrile-d_3 (PS or OS–MHS) ([C] = 0.5 mol/L).

in the O(E)S system is not clear, the electron-accepting ability of O(E)S may be lower than that of P(E)S or stacking may be sterically controlled in the case of O(E)S.

Occurrence of C–T stacking as one of the two interactions in the case of P(E)S can be confirmed by using a phenol derivative having a bulky substituent because the bulky

Table IV. Change of IR Carbonyl Absorption of PS and OS by Addition of Phenols[a]

monomer	phenol	$\nu_{C=O}$ (cm^{-1})	$\Delta\nu_{C=O}$ (cm^{-1})	interaction
PS	none	1684		
PS	phenol	1636	48	HB[b] + CTS[c]
PS	*p-tert*-butylphenol	1655	29	HB[b]
OS	none	1748		
OS	phenol	1719	29	HB[b]
OS	*p-tert*-butylphenol	1719	29	HB[b]

[a] Eight equiv of phenol was added to PS or OS at 25 °C. [b] HB: hydrogen bonding. [c] CTS: C–T stacking.

group may sterically prevent the stacking between the pyrrolidone and phenol groups. Actually, such behavior was observed in the case of bifunctional pyrrolidones in the previous study.[9] When the shift of IR carbonyl absorptions of PS and OS by addition of phenol and *p-tert*-butylphenol (8 equiv) was examined, the results summarized in Table IV were obtained. The carbonyl absorption of PS was shifted to a 48 cm^{-1} lower frequency by addition of phenol, while that of OS was shifted to 29 cm^{-1}. By the addition of *p-tert*-butylphenol the shift of PS carbonyl dropped to 29 cm^{-1}; however, that of OS carbonyl was not changed (29 cm^{-1}). This result, as the authors predicted, clearly indicates that C–T stacking takes place in the system of P(E)S–MHS but not in the system of O(E)S–MHS. Therefore, the difference in strength of the interaction with phenol group between pyrrolidone and oxazolidone groups depends on the presence of C–T stacking. It is conceivable that the synergistic effect of hydrogen bonding and C–T stacking generates a stronger interaction between pyrrolidone and phenol groups than between oxazolidone and phenol groups, resulting in the higher alternating copolymerizability in the P(E)S–MHS system.

In this paper, alternating copolymerizability enhanced by molecular interaction between pyrrolidone and phenol groups was demonstrated. The interaction consisted mainly of hydrogen bonding and C–T stacking between the two groups by way of contrast with results obtained with O(E)S.

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