Copolymerization of Styrene and Methacrylic Acid in the Presence of Poly(2-vinylpyridine) as the Template

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ABSTRACT: We have studied, using ^{1}H and ^{13}C NMR, the effects on solution radical polymerization of styrene (ST) with methacrylic acid (MA) in the presence of a homogeneous, high molecular weight ($\bar{M}_w = 2 \times 10^5$), poly(2-vinylpyridine) (P2VP) template. The presence of the template had little, if any, effect on the molecular weight, composition, or glass transition temperatures of the copolymers but produced copolymers with significantly longer block lengths of both ST and MA repeat units.

Introduction

Template effects on radical polymerization have been studied widely by many researchers,[1-7] and such template effects have been observed on the rate of polymerization, the molecular weight, and the stereoregularity of the polymers. However, the template effects in copolymerization have been less frequently studied. The rate of template copolymerization of styrene (ST) and methyl methacrylate (MMA) was studied in the presence of isotactic poly(methyl methacrylate) (PMMA).[8] The template also affected the reactivity ratios of the monomers in the copolymerization of ST and acrylonitrile multimethacrylates, ST/MA (methacrylic acid for MA) and MMA/MA with poly(ethylene glycol) as the template.[9,10] Template copolymerization effects on the structure of the co-condensation polymers of poly-L-alanine NCA (*N*-carboxyanhydride) and sarcosine-NCA were observed for the first time by using NMR techniques.[11] Several factors make the study of template copolymerization more difficult. First, the rate enhancements that were generally observed in most template polymerizations were not observed in some template copolymerization systems.[8] Second, it is difficult to separate the copolymer from the template,[12] and hence the characterization of the pure copolymer structure is difficult. Third, the overlap of the peaks in the NMR spectrum of the copolymer due to different sequences and different costereoregularity in most copolymer systems makes it more difficult to assign and analyze the spectral lines. In this paper we report the results of the poly(2-vinylpyridine) (P_2VP, $\bar{M}_w = 2 \times 10^5$) template copolymerization of ST and MA using benzoyl peroxide (BPO) as the initiator. The triad sequences of the copolymer were assigned and the sequence distribution was studied.

Experimental Section

1. **Materials.** The description of the raw materials used is listed in Table I. ST and MA monomers were distilled under partial vacuum in a N_2 atmosphere. BPO was dried under vacuum at room temperature and stored in a desiccator. Poly(2-vinylpyridine) was used without further purification. Toluene and acetone were refluxed over CaH_2 for 6 h and then distilled and stored over 4-Å molecular sieves before use.

2. **Synthesis of Copoly(ST/MA).** The copolymerizations of ST and MA at different monomer ratios were carried out at 70 °C in a N_2 atmosphere for 24 h. A mixture of toluene and acetone in the ratio of 4:1 by volume was used as the solvent for all the systems because there was less interaction of this solvent with the monomers and the template. The molar ratio of monomer to initiator was 75:1. The monomer concentration was 0.8 M. The copolymers were precipitated in petroleum ether, then washed with petroleum ether several times, and dried under vacuum at 60 °C for 24 h. The final copolymers were white powders.

Table I
Materials Employed and Their Abbreviations

designation	name and description	source
P2VP	poly(2-vinylpyridine), $\bar{M}_w$ = 200 000	Polysciences, Inc.
MA	methacrylic acid	Aldrich
ST	styrene	Aldrich
BPO	benzoyl peroxide (99%)	Aldrich
acetic acid, glacial	reagent A.C.S.	Fisher Scientific
toluene	solvent grade	Aldrich
petroleum ether	solvent grade	Aldrich

3. **Synthesis of Copoly(ST/MA) in the Presence of P2VP.** The copolymerization of ST and MA in the presence of P2VP was carried out in a similar way as employed in the previous section, but P2VP, which has a specific interaction with MA and so a kinetic template effect on the polymerization of MA,[13] was introduced into the reaction mixture at the beginning at a monomer to P2VP molecular ratio of 6:1 based on pyridine unit. Other conditions were exactly the same as those used in section 2. The complexes of copoly(ST/MA) with P2VP were formed during the copolymerization. The complex was then precipitated and washed with petroleum ether several times and dried in vacuum at 60 °C for 10 h. The separation of the copolymer from P2VP was carried out by extraction with acetic acid at room temperature for 120 h (and for each 24 h the acetic acid employed in the extraction was replaced by fresh acetic acid). Longer time of extraction was used for separating the copolymers with higher MA content. The completion of separation was checked by the ^{1}H-NMR spectra. The copolymer was filtered and washed with petroleum ether and then dried under vacuum at 60 °C for 24 h. The copolymer was a white powder or was composed of white granules depending on the copolymer composition.

Characterization

1. **Gel Permeation Chromatography (GPC).** The relative molecular weight of the copolymer of ST and MA was obtained from a GPC measurement (Waters Maxima 820; eluant, tetrahydrofuran; column, polystyrene; length, 30 cm; void volume, 12 min; flow rate, 1 mL/min at 25 °C). Standard PMMA samples were used to obtain the universal calibration curve.

2. **Differential Scanning Calorimetry (DSC).** The glass transition temperatures (T_g's) of the copolymer samples were determined by DSC (Du Pont 2910 DSC). DSC measurements were carried out with 10-mg samples in the temperature range 25–280 °C at the scanning rate of 20 °C/min under a N_2 atmosphere.

3. **NMR Measurements.** ^{1}H-NMR and ^{13}C-NMR spectra were obtained from XL-300 and GN-500 NMR instruments. Deuterated dimethylformamide (DMF-d_7) was used as the solvent and $(CH_3)_4Si$ was used as the

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Table II
Characteristics of Copoly(ST/MA) (Nontemplate System)

run	feed comp, ST mol %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_g, °C	copolymer comp, ST mol %	conversion, %
1	0	58 600[a]			0	
2	8.7			198[c]	7.7 ± 0.6	82
3	27	29 600	11	177	24 ± 0.8	
4	46	24 400	11	160	50 ± 1.2	70
5	60	11 600	3.2	163	53 ± 0.7	80
6	67	11 300	>12	156	55 ± 0.9	72
7	73			161	61 ± 0.8	73
8	89			106	89 ± 0.7	71
9	100	13 000[b]		100	100	

[a] Determined by viscosity method.[15] Solvent: 0.002 N HCl. $K = 66 \times 10^{-4}$. $a = 0.5$. Temperature: 30 °C. [b] Determined by viscosity method.[15] Solvent: toluene. $K = 8.48 \times 10^{-5}$. $a = 0.748$. Temperature: 25 °C. [c] There is some doubt if these values are due simply to the glass transitions and may involve already partial dehydration of the polymer.

reference. The ^{13}C-NMR spectra were obtained at the frequency of 75.5 MHz with ^{1}H decoupling and 15% by weight solutions were used. NOE was minimized by choosing a decoupling mode and long delay time ($D1$). The compositions of the copolymer were determined on the basis of the aromatic group region and the methyl group region of the ^{1}H-NMR spectra. The compositions were checked by a UV method.[14] The errors between the two measurements were within ±4%.

Results and Discussion

A series of copolymerization runs of ST/MA with different monomer feed ratios were performed without template. The results are listed in Table II. As the feed ratio changes, the compositions of the copolymers formed also change. Generally, the amount of ST units in the copolymer was slightly less than the feed ratio. The glass transition temperature varies as the composition changes. The fewer ST units in the copolymer, the higher the T_g of the sample. The number-average molecular weight of the copolymers does not change very much as the feed ratio or composition of the copolymer changes, and the molecular weight distribution is very broad for almost all the feed ratios employed. The too broad molecular weight distribution may be due to the unstable base line of the GPC curve.

We will first interpret the proton NMR spectra on the basis of a chemically motivated ansatz and assume the simple first-order Markov statistics to compute the intensity of the principle ^{1}H-NMR lines (which was applied to copolymer seqeunce analysis by F. A. Bovey[17]). Excellent agreement was obtained between the predicted and the observed intensities. These assignments are further confirmed qualitatively by comparison of the major ^{13}C-NMR lines. We do not have sufficient ^{13}C-NMR data on both polymers and oligomers to make a fully quantitative comparison.

We first assign the triad sequences of the ^{1}H-NMR spectrum in the methyl group region. Careful examination of the ^{1}H-NMR spectra shows that the methyl group peaks are sensitive to the triad sequences of the copolymers. A typical spectrum is shown in Figure 1. In the methyl region, we observed three main peaks located at three regions called A, B, and C, which are assigned later as three M-centered triads MMM, MMS, or SMM and SMS, respectively (where M refers to MA and S refers to ST). This assignment was based on the following facts: First, methyl resonances due to pure radical-initiated polymethacrylic acid (PMA) were all located in the A region.

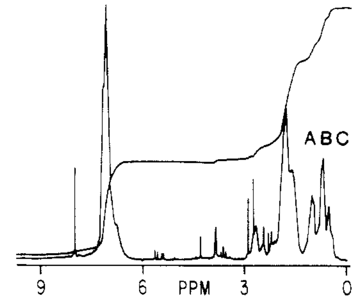

Figure 1. ^{1}H-NMR spectrum of copoly(ST/MA) from the nontemplate system (composition in molar ratio ST/MA = 50/50).

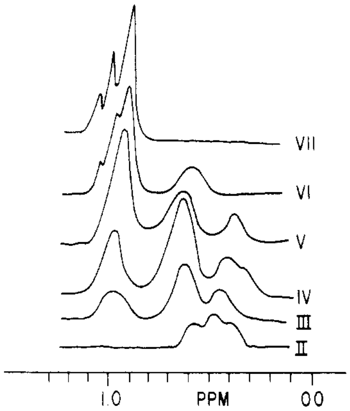

Figure 2. ^{1}H-NMR spectra of copoly(ST/MA) with different compositions in the methyl resonance region for compositions (molar ratio ST/MA): II, 89/11; III, 54/46; IV, 50/50; V, 24/76; VI, 8/92; VII, 0/100.

Resonances of the copolymer at B and C regions must correspond to triad sequences MMS or SMM and SMS. Second, methyl resonances of copolymers with different composition are shown in Figure 2. We expect that the triad sequence composition will change as the composition of the copolymer changes because, in the free radical copolymerization of ST and MA, the monomers have a similar reactivity ratio of, e.g., $r_{ST} = 0.55$, $r_{MA} = 0.39$.[15] With less ST units in the copolymer chain, we should observe less of the SMS sequence. It is also reasonable to expect less MMM sequences for those copolymers with fewer MA units. This is perfectly demonstrated by the spectra in Figure 2. Further, we assume no peak overlap between three triad sequences despite the reported fact that the presence of an aromatic ring in the copoly(MMA/ST) has a significant effect on the chemical shifts of the methoxyl and methyl regions.[16] With these tentative assignments we can make a statistical prediction of the intensities of the NMR lines, which can be compared with observations.

Let F_1 and F_2 be the unconditional probabilities of finding a methacrylic acid unit and a styrene unit in the copolymers, respectively. We define the following probability parameters P_{ij}, i, j = 1, 2, for each of the possible reactions shown below:

$$\mathrm{M} + \mathrm{M}^{\bullet} \xrightarrow{P_{11}} \mathrm{M}^{\bullet}$$

$$\mathrm{M} + \mathrm{S}^{\bullet} \xrightarrow{P_{21}} \mathrm{M}^{\bullet}$$

$$\mathrm{S} + \mathrm{M}^{\bullet} \xrightarrow{P_{12}} \mathrm{S}^{\bullet}$$

$$\mathrm{S} + \mathrm{S}^{\bullet} \xrightarrow{P_{22}} \mathrm{S}^{\bullet}$$

Table III
Observed and Predicted Triad Sequence Intensities for Copoly(ST/MA)

	4 ST mol % = 50 P_{11} = 0.59 P_{22} = 0.59		5 ST mol % = 53 P_{11} = 0.63 P_{22} = 0.67		6 ST mol % = 55 P_{11} = 0.57 P_{22} = 0.65		7 ST mol % = 61 P_{11} = 0.55 P_{22} = 0.71	
copolymer sequence	obs	pred	obs	pred	obs	pred	obs	pred
[MMM]	0.17	0.17[a]	0.186	0.186[a]	0.146	0.146[a]	0.120	0.120[a]
[SMM]	0.23	0.24	0.220	0.220	0.212	0.220	0.185	0.185
[SMS]	0.10	0.08	0.064	0.065	0.088	0.083	0.087	0.079

[a] These values follow directly from eq 2 where they are the bases for finding the probabilities P_{11} and P_{22}.

Table IV
Characteristics of Copoly(ST/MA) (Template Systems)

run	feed comp, ST mol %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_g, °C	copolymer comp, ST mol %	conversion, %
3T	27			195[a]		
4T	46			164	54 ± 0.4	82
5T	60	21 000	2.9	189	41 ± 1.1	80
6T	67	15 000	3.4	188	47 ± 0.6	70
7T	73			180	63 ± 0.7	63
8T	89			106	90 ± 1.0	60

[a] There is some doubt if this value is due simply to the glass transition and may involve already partial dehydration of the copolymer.

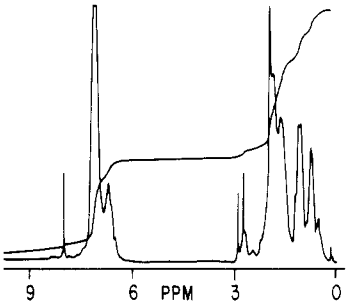

Figure 3. ^{1}H-NMR spectrum of copoly(ST/MA) from the P2VP template system (composition molar ratio ST/MA = 54/46).

The following relations must apply[17]

$$P_{11} + P_{12} = 1 \quad \text{and} \quad P_{22} + P_{21} = 1 \qquad (1)$$

Thus for M-centered triads that give methyl proton NMR signals, we find that[17]

$$[\mathrm{MMM}] = F_1 P_{11}^{\,2}$$

$$[\mathrm{MMS}] = F_1 P_{11}(1 - P_{11}) + F_2(1 - P_{22})P_{11} \qquad (2)$$

$$[\mathrm{SMS}] = F_2(1 - P_{22})(1 - P_{11})$$

$$F_1 = [\mathrm{MMM}] + [\mathrm{MMS}] + [\mathrm{SMS}]$$

$$F_1(1 - P_{11}) = F_2(1 - P_{22})$$

We found, e.g., [MMM] = 0.186, [SMS] = 0.064 in system 5 where F_1 = 0.47, F_2 = 0.53, hence $P_{11} = ([\mathrm{MMM}]/F_1)^{1/2} = (0.186/0.47)^{1/2} = 0.63$; similarly $1 - P_{22} = [\mathrm{SMS}]/[F_2(1 - P_{11})] = 0.064/[0.53(0.37)]$, or P_{22} = 0.67.

The comparison of observed and calculated results for our systems is shown in Table III. The agreement supports both our line assignments and the assumption of the first-order Markov statistics, which has previously been applied to this system.[10]

Template Effect. The characteristics of various template copoly(ST/MA) samples prepared by us are shown in Table IV. By comparing these numbers with those in Table II, it is obvious that there is not too much difference in $\bar{M}_n$'s, composition, and T_g's of these copolymers. However, we see significant differences in the ^{1}H-NMR spectra of the template and nontemplate systems. Typical ^{1}H-NMR spectra are shown in Figure 3. The methyl group resonance shows a larger tendency to form blocks of the copolymer chains formed in the systems containing the template (P2VP). The same statistical calculations (see eqs 1 and 2) were used and consistency was also found in the template systems. The results are shown in Table V. Both probabilities P_{11} and P_{22} were found to be significantly larger than those in the nontemplate systems, thus the average length of ST and MA blocks of the copolymers should be larger in template-containing systems. Table VI shows the probabilities and the calculated[17] average sequence length of MA and ST units in copolymers from both template and nontemplate systems.

Although the detailed assignment of the ^{13}C-NMR spectral lines is not possible because of the overlap of the peaks as well as the lack of the information from model copolymers, we still observe the differences between the relative intensities of the copolymers from the template and the nontemplate systems. These differences are shown in Figure 4 (trace I for the template system and trace II for the nontemplate system) where the two copolymers have a similar composition. These differences are actually a further indication of what we have observed in the ^{1}H-NMR spectra where they show that longer blocks are present in the copolymers synthesized in the presence of a template. By studying the ^{13}C-NMR spectra of the copoly(ST/MA) with different composition, which are shown in Figure 5, we learn that the chemical shift changes

Table V
Observed and Predicted Triad Sequence Intensities for Copoly(ST/MA) (Template Systems)

	4T ST mol % = 54 P_{11} = 0.72 P_{22} = 0.76		5T ST mol % = 41 P_{11} = 0.83 P_{22} = 0.75		6T ST mol % = 47 P_{11} = 0.80 P_{22} = 0.77		7T ST mol % = 63 P_{11} = 0.82 P_{22} = 0.89	
copolymer sequence	obs	pred	obs	pred	obs	pred	obs	pred
[MMM]	0.24	0.24[a]	0.403	0.403[a]	0.345	0.345[a]	0.249	0.249[a]
[MMS]	0.17	0.19	0.159	0.168	0.158	0.171	0.104	0.112
[SMS]	0.05	0.04	0.029	0.017	0.030	0.021	0.021	0.012

[a] These values follow directly from eq 2 where they are the bases for finding the probabilities P_{11} and P_{22}.

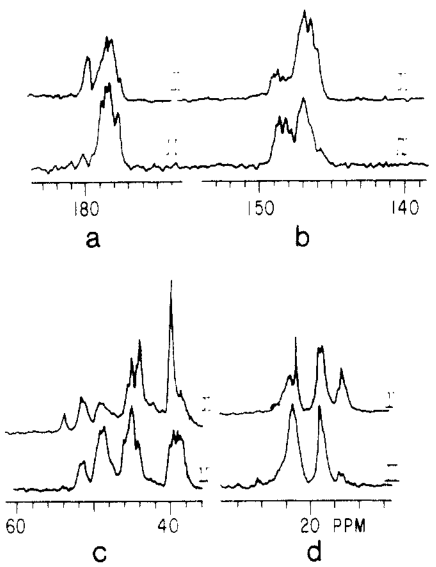

Figure 4. ^{13}C-NMR spectra of copoly(ST/MA). Pulse width, 11 μs; delay time, 3 s; number of scans, 25 000. (I) From the P2VP template system (composition: molar ratio ST/MA = 63/37). (II) From the nontemplate system (composition: molar ratio ST/MA = 61/39). (a) Carbonyl resonance; (b) aromatic quaternary carbon resonance; (c) methylene and methine resonance; (d) methyl resonance.

Table VI
Statistical Probabilities and Average Sequence Lengths for Template and Nontemplate Systems

	comp, mol %		probabilities		av sequence length	
copolymers	MA	ST	P_{11}	P_{22}	N(MA)	N(ST)
4	0.50	0.50	0.59	0.59	2.44	2.44
4T	0.46	0.54	0.72	0.76	3.57	4.17
5	0.47	0.53	0.63	0.67	2.70	3.03
5T	0.59	0.41	0.83	0.75	5.88	4.00
6	0.45	0.55	0.57	0.65	2.33	2.86
6T	0.54	0.47	0.80	0.77	5.00	4.35
7	0.39	0.61	0.55	0.71	2.22	3.45
7T	0.37	0.63	0.82	0.89	5.56	9.09

for some sensitive group peaks, e.g., carbonyl carbons and aromatic quaternary carbons. In the carbonyl resonances, more [SMS] sequences are expected in trace II of Figure 5 because the copolymer contains more ST unit. The peaks between 176 and 179 ppm are mainly due to [SMS] sequences of the copolymer, while the peaks between 180 and 182 ppm are mainly due to [MMM] sequences. By the same reasoning we analyze the aromatic quaternary carbon resonance. The peaks between 145 and 146.5 ppm are mainly due to [SSS] sequence and those peaks between 146.5 and 148 ppm are mainly due to [MSM] sequence. In Figure 4, the carbonyl resonances indicate that more [MMM] sequences are present in the copolymer from the template system (trace I) than that of the copolymer from the nontemplate system (trace II) because of the presence of the peaks at 180–182 ppm in trace I, while the aromatic quaternary resonances indicate that more [SSS] sequences are present in the copolymer from the template system (where the two copolymers have a similar composition). These observations are only explained by the presence of longer MA blocks and longer ST blocks in the copolymer synthesized in the presence of the template. This characteristic is also observed in methylene and methine resonances. In the methylene region, pure PMA has two peaks at 55 and 52.5 ppm. Pure PS has peaks in 42–50-ppm region. In the ST/MA copolymer, the [SM] diad sequence should be at 48–54 ppm, where they overlap with the [SS] and [MM] sequences to some extent. However, the peak at 55 ppm is a strong indication of the presence of the [MM] sequence. Similarly, PS has peaks at 40 ppm corresponding to the CH group. With an increase of MA content in the copolymer, the peaks were further split by the sequences [SSS], [SSM], and [MSM]. A strong, sharp peak remains in the copolymer with a low MA content. This peak should be due to the [SSS] sequence. In Figure 4c, trace I (template system) shows this pattern (peaks at 55 and 40 ppm) and indicates that more [MM] and [SSS] sequences are present in the copolymer from the template systems.

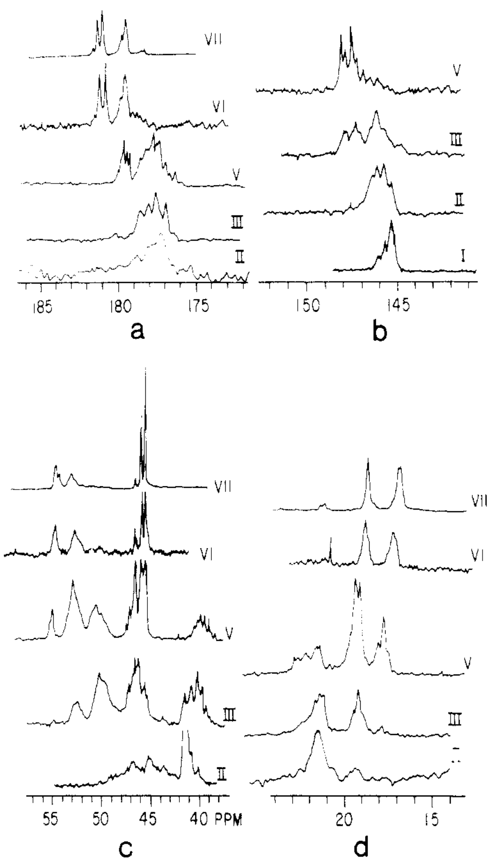

Figure 5. ^{13}C-NMR resonances of copoly(ST/MA) with different compositions. Pulse width, 11 μs; delay time, 3 s; number of scans, 25 000–28 000; molar ratio ST/MA (I) 100/0, (II) 89/11, (III) 50/50, (V) 24/76, (VI) 8/92, (VII) 0/100. (a) Carbonyl resonance; (b) aromatic quaternary resonance; (c) methylene and methine resonance; (d) methyl resonance.

We conclude that the addition of the P2VP template to the copolymerization of MA/ST leads to copolymers with longer average ST and MA sequences but does not strikingly affect the composition, $\bar{M}_n$, or T_g. A similar sequence effect was previously observed with cocondensation polymers.[11]

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Registry No. ST/MA (copolymer), 9010-92-8; PS (homopolymer), 9003-53-6; PMM (homopolymer), 25087-26-7; P_2-VP (homopolymer), 25014-15-7.