Microstructures of Styrene–Acrylamide Copolymers Using ^{13}C NMR Spectroscopy

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ABSTRACT: The microstructures of poly(styrene-*co*-acrylamide)s of varying compositions, prepared by solution polymerization of styrene with *N,O*-bis(trimethylsilyl)acrylamide, followed by deprotection, were studied by ^{13}C NMR. Sequence distributions of monomers analyzed from triad proportions were found to confirm Bernoullian statistics within experimental error. The glass transition temperature (T_g) of various copolymers was obtained from Barton's equation (using diad relation) and in good agreement with those determined by differential scanning calorimetry. T_g values of alternating styrene–acrylamide copolymers were calculated.

KEY WORDS *N,O*-Bis(trimethylsilyl) Acrylamide / Microstructure / ^{13}C Nuclear Magnetic Resonance / Solution Polymerization / Sequence Distribution / Glass Transition Temperature /

Functional polymers with properties conferred by high molecular weight of the polymers are combined with those derived from the presence of specific functional groups. Suitably protected acrylamides reduced hydrogen bonding should improve solubility in organic solvents. Interestingly changes in reactivity during copolymerization with styrene were noted. Literature reveals that copolymerization of acrylamide with hydrophobic styrene monomers produces copolymers which are blocky, i.e., compositionally inhomogeneous in nature. It is believed that properties of copolymers, in particular, of those containing polar and non-polar monomers can be improved by decreasing compositional inhomogeneity.¹ A new compositionally homogeneous copolymer of styrene and acrylamide has been reported recently,^{2,3} derived from a solution copolymerization of styrene with a protected acrylamide, namely, *N,O*-bis(trimethylsilyl)-acrylamide (BTSAm), followed by deprotection of silyl group. This method provides for the first time, a range of copolymer compositions, hitherto inaccessible. Hence it is of interest to examine the microstructure and statistics of this copolymerization using ^{13}C NMR spectroscopy. Although a variety of copolymers of acrylamide (acrylamide–acrylic acid),^{4–7} trimellitic anhydride-*co*-imides,⁸ and styrene (styrene–methacrylate,⁹ styrene–methacrylonitrile¹⁰) has been studied by ^{13}C NMR spectroscopy, there is no report in the literature on poly(styrene-*co*-acrylamide)s.

EXPERIMENTAL

The copolymers of styrene and acrylamide, with varying feed compositions were prepared in low conversions by methods previously described² (Table I). These copolymers were used for NMR study. ^1H NMR spectra were recorded with 200 MHz (Bruker AC-200) spectrometer at 298 K, by using dimethylsulfoxide- d_6 (DMSO- d_6) as the solvent and locking agent.

^{13}C NMR spectra recorded at 75.48 MHz (Bruker MSL-300) spectrometer at 373 K. Sample concentration was 12% w/v DMSO- d_6 . Spectra were obtained using

a BROADBAND decoupling and pulse delay of 10 s, accumulating 6000 scans with a digital resolution of 0.4 Hz/point, corresponding to a spectral width 25000 Hz and a data length of 8 K. The flip angle and acquisition time was 45° and 1.3 s, respectively. Monomer sequence placements were determined by comparing relative peak areas of the proton or carbon atoms. In performing quantitative NMR measurements *via* compositional or configurational sequence placements, one must take into account differences in the Nuclear Overhauser Effect (NOE) and spin-lattice relaxation times (T_1). No NOE or T_1 have been determined but one additional ^{13}C NMR experiment was performed on a copolymer B-63 with a much longer delay (15 s) and gating off the decoupler to remove the NOE. The results are identical with those obtained *via* ^{13}C NMR spectra with the standard method. We assumed that no differential T_1 's are present for compositional triads (AAA, AAS, SAS, SSS, etc.) in the ^{13}C NMR spectra. No differential ^1H NOEs were considered to occur. Relative peak areas were proportional to the numbers of proton and carbon atoms. Peak areas were determined by deconvolution method using Bruker WIN-NMR software.

The thermal properties of the styrene–acrylamide copolymers were determined using Perkin-Elmer DSC-7 thermal analyzer. Glass transition temperatures were determined from thermograms at the points of inflexion.

THEORY

The essentials of the statistics of copolymerization, with reference to the present problem have been reported.^{11,12} Let S and A denote styrene and acrylamide units, respectively. The relative proportions of monomer, diad and triad sequence are related as in the literature.

In the Bernoullian model there is one independent probability, that of adding, say, an S unit, P_S . Necessarily, $P_S + P_A = 1$. The monomer and triad intensities are related to P_S by

$$(\text{SSS}) = P_S^3 \quad (\text{SAS}) = P_S^2(1 - P_S)$$

$$(\text{SSA}) = 2P_S^2(1 - P_S) \quad (\text{AAS}) = 2P_S(1 - P_S)^2$$

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$$(ASA) = P_S(1 - P_S)^2 \quad (AAA) = (1 - P_S)^3$$

This model implies the existence of only two propagation steps.

giving

$$P_S = rf_S / [1 + f_S(r - 1)]$$

Where $r = k_S/k_A$ and f_S is the mole fraction of S in the comonomer feed.

In the first-order Markov model, addition probability depends on the end unit of the growing chain. There are four conditional probabilities, P_{XY} , where X denotes the end unit and Y the added unit (X, Y = S or A). Only two probabilities are independent since necessarily $P_{SS} + P_{SA} = P_{AA} + P_{AS} = 1$.

Defining $u = P_{SA}$ and $w = P_{AS}$, one obtains.

$$(SSS) = w(1 - u)^2 / (u + w)$$

$$(SSA) = 2uw(1 - u) / (u + w)$$

$$(AAS) = 2uw(1 - w) / (u + w)$$

$$(ASA) = u^2w / (u + w)$$

$$(AAA) = u(1 - w)^2 / (u + w)$$

$$(SAS) = uw^2 / (u + w)$$

This model corresponds to four distinct propagation steps of the general form:

giving

$$u = (1 - f_S) / [1 + f_S(r_S - 1)] \quad \text{and} \quad w = f_S / [r_A + f_S(1 - r_A)]$$

where r_S and r_A (the reactivity ratios) are equal to k_{SS}/k_{SA} , and k_{AA}/k_{AS} , respectively. If $r_S = r_A = 1$ (and hence $P_{SA} + P_{AS} = 1$), first-order Markov statistics reduces to the Bernoullian case.

RESULTS AND DISCUSSION

Various copolymer samples in the present study are shown in Table I. The copolymer compositions were determined by ^1H NMR (200 MHz) spectroscopy. The only solvent giving clear solution for a wide range copolymer compositions was dimethyl sulfoxide (DMSO). Peaks sensitive to configurational effects of styrene-acrylamide copolymers overlapped in the region (30–40 ppm) with DMSO- d_6 (solvent) peaks. Hence, compositional effects were considered more sensitive than configurational effects. For sequence analysis, resonance signals of homopolymers, polystyrene (PS), polyacrylamide (PA) and copolymers S/A were considered.

Figure 1(a, b, c) shows the resonance signals of homopolymers, PA in D_2O at 70°C , PS in 1,2,4-trichloro benzene at 100°C and S/A copolymer (B-82). Previous NMR studies,^{13–15} of acrylamide (A) homopolymer

Table I. Copolymer feed compositions (mol%)

	B-30	B-63	B-82	B-91
Styrene	71.3	37.1	17.7	8.8
BTSAm	28.7	62.9	82.3	91.2
Intrinsic viscosity ^a $[\eta]$ /dl gm ⁻¹	0.20	0.21	0.27	0.31

^a Determined in DMSO at $30 \pm 0.1^\circ\text{C}$.

Figure 1. (a) 300-MHz ^{13}C NMR spectrum of a low-conversion solution of styrene (S)-acrylamide (A) copolymer (B-82) in DMSO- d_6 at 100°C . (b) Polystyrene in 1,2,4 trichloro benzene at 100°C . (c) Polyacrylamide in D_2O at 70°C .

have shown that the C=O peak is essentially unaffected by tacticity, whereas C_α resonances are split by configurational triad (or pentad) effects and C_β resonances by configurational hexad effects. For PS, a sharp singlet centered around $\delta 40.8$ ppm can be assigned to $(\text{CH})_S$. The methylene carbon atom shows a multiplet in the range of $\delta 43.0$ – 46.0 ppm which shows sensitivity toward tacticity. A highly complex aromatic ring-carbon resonance pattern is exhibited by C-1 around $\delta 145.0$ – 146.10 ppm whereas around $\delta 145.0$ – 146.10 ppm the C-1 carbon (quaternary carbon of the aromatic ring) exhibits complex configurational effects^{16,18} with pentad sensitivity. There is no splitting for *ortho*-, *meta*-, and *para*-carbon which appeared around $\delta 128.6$, 127.2 , and 126.0 ppm, respectively. Based on this, peak assignments were made for PS and PA homopolymer in the present study. The aromatic carbon atoms in PS show splitting depending on the environment. S/A copolymers of various compositions, obtained using BTSAm, exhibit

Table II. Composition of styrene (f_s), copolymer composition (F_s), degree of conversion (Y), and triad relative intensities of copolymers derived from styrene and BTSAm

System	$Y/\%$	f_S	f_A	F_S	F_A	$T_1/^\circ\text{C}^a$	Relative intensity						
							SSS	SSA	ASA	SAS	AAS	AAA	
B-30	9.2	0.713	0.287	0.709	0.291	100	Exptl	0.356	0.294	0.056	0.146	0.125	0.023
							B ^b	0.356	0.293	0.060	0.146	0.120	0.025
							M ^c	0.356	0.292	0.059	0.145	0.122	0.025
B-63	10.0	0.371	0.629	0.568	0.432	100	Exptl	0.183	0.279	0.107	0.139	0.212	0.080
							B ^b	0.183	0.279	0.106	0.139	0.212	0.081
							M ^c	0.193	0.277	0.099	0.131	0.213	0.087
B-82	9.7	0.177	0.823	0.306	0.694	100	Exptl	0.026	0.125	0.147	0.066	0.296	0.334
							B ^b	0.029	0.130	0.147	0.065	0.295	0.334
							M ^c	0.025	0.124	0.151	0.065	0.296	0.336
B-91	8.5	0.088	0.912	0.286	0.714	100	Exptl	0.023	0.114	0.144	0.058	0.268	0.367
							B ^b	0.023	0.117	0.146	0.058	0.292	0.364
							M ^c	0.022	0.118	0.151	0.062	0.295	0.349

^a Temperature of NMR spectrum scanning. ^b Bernoullian. ^c Markov.

highly complex aromatic ring-carbon resonance patterns around 142.0–144 ppm. No splitting was observed for *ortho*-, *meta*-, and *para*-carbon which appeared around 143.0–144.0 ppm, while no splitting was observed for *ortho*-, *meta*-, and *para*-carbon; for S/A copolymers the resonance 128.0, 127.0, and 124.0 ppm, respectively. Signals around 30–38 ppm were assigned to $(\text{CH})_A$, $(\text{CH}_2)_A$, but could not be used for sequence analysis because of overlap with the signals of the solvent. The signals in the region 38–42 ppm are assigned to $(\text{CH})_A$, $(\text{CH})_S$ and $(\text{CH}_2)_S$ but cannot be used for sequence analysis due to the overlap of the signals from both monomeric units. The sharp signals around 128.0, 126.0, and 124.0 ppm can be attributed to *ortho*-, *meta*-, and *para*-carbon atoms of the phenyl ring, respectively, indicating insensitivity toward different compositional sequences.

The C-1 carbon of the styrene unit appeared as a well-resolved multiplet in the region 141 to 144 ppm, indicating sensitivity towards different monomer placements. The carbonyl carbon signal in the S/A copolymer appeared as a multiplet around 174 to 176 ppm indicating sensitivity towards different compositional sequences. In case of the S/A copolymer, a shift in the position of various functional groups of the units from S and A was observed (in comparison to homopolymers). This was due to the change in the nature of adjacent monomeric units in the copolymer which changes the chemical shift of S and A centered triads.

The carbonyl $(>\text{C}=\text{O})_A$ (A) and $(\text{C}-1)_S$ carbon (B) regions of S/A copolymers are shown in Figure 2(a, b, c, and d). The chemical shift difference within the resonance signals and the splitting pattern shows sensitivity toward different monomer sequences and co-tacticity in the carbonyl carbon resonances. PA exhibits a singlet around 181.0 ppm. As styrene in the sample increases, signal characteristics of the polymer decreases, whereas a set of up field signals centered between 174.5 and 175.5 ppm starts to appear. Three sets of signals, the intensities of which change with copolymer composition, can be assigned to the carbonyl carbon atom of the central unit from A in SAS, SAA(AAS), and AAA triad sequence from low to high field. In the case of A-centered triads, introduction of a unit from S in a

AAA triad causes downfield shift in the positions of the SAA (by δ 0.40 ppm) and SAS signals (by δ 0.50 ppm). Van Doremaelae *et al.*⁹ have reported a similar type of assignment for styrene/methyl acrylate copolymers. Concentration of various A-centered triads can be calculated from the relative areas of respective signals.

Poly(styrene-*co*-acrylamide)s were prepared at low conversions (10%). The characteristics of the samples are given in Table II. The mole fractions of styrene in the feed (f_s) and that in the final copolymer (F_s) are reported together with the percentage conversion (Y). The results for sample B-30 obtained from BTSAm (Table II) show an excellent agreement between f_s and F_s . Such agreement is expected logically for $Y=100\%$. For more detailed insight into copolymerization kinetics, the sequence distribution as revealed by the triad proportions was examined.

Figure 2 shows the development of the carbonyl resonance of acrylamide and *ipso* carbon C-1 of styrene with increasing acrylamide content for the copolymer B-30, B-63, B-82, and B-91. ¹³C NMR spectra of carbonyl and C-1 carbon for S/A copolymer samples B91 and their deconvolution are shown in Figure 2. Numerical data are given Table II. The spectra of the homopolymers, PS and PA are also shown in Figure 1 for comparison, and the triad assignment is indicated on the spectrum of B-82. This assignment was deduced directly from the dependence of the component resonance on copolymer composition and a comparison with the homopolymer chemical shifts. The assignment is also in agreement with those reported previously for radical poly(acrylamide-*co*-acrylate)s prepared in water⁶ and in inverse micro emulsions using oil–water system.⁸

Deconvolutions were performed for the carbonyl peak of the acrylamide group. For deconvolution the peak positions are the same as those determined experimentally for B91 (*i.e.*, 174.9 ppm for SAS triad, 174.7 ppm for AAS/SAA triad, and 174.5 ppm for AAA triad). For each sample, line width is determined on the AAA peak, which displays the best resolution and we assume that all triads of a given sample have the same line width: a very classical assumption for such systems. Then we have to adjust coefficients of each triad to obtain the best fit with the experimental data. In this process, the initial

Figure 2. Expanded 300-MHz ^{13}C spectra of B-30, B-63, B-82, and B-91, showing only the carbonyl region (174–177 ppm) and the quaternary aromatic carbon region (174–177 ppm) and quaternary aromatic carbon region C-1 *ipso* (141–147 ppm). Spectra were recorded in $\text{DMSO}-d_6$ at 100°C . Area measurements have been performed by using WIN-NMR software.

value of the peak position appears critical (± 0.05) and the line width has to be defined at ± 2 Hz. This leads to an accuracy of about 5% of the value of each coefficient. Similarly, the C-1 peak positions are the same as those determined experimentally for B30 (*i.e.*, 144.1 ppm for SSS triad, 143.4 ppm for SSA/ASS triad, and 143.2 for ASA triad). For each sample, the line width is determined on the SSS peak, which displays the best resolution and we assume that all triads of a given sample have the same line width. This also leads to accuracy of about 5% of the value of each coefficient. The peak positions have also been reported.^{5,16} Deconvolution of the carbonyl and C-1 carbon peaks in S/A copolymers, have been performed and Table II shows that deconvolution results are in good agreement with Bernoullian statistics.

Figures 3 and 4 show a comparison between experimental triad proportions and theoretical distribution curves for Bernoullian statistics calculated using the relationship $P_S = F_S$. Literature values of reactivity ratios differ from unity. However, there is surprisingly good agreement between experiment and theory. Truong *et al.*⁶ has also shown that for high conversion, apparent distribution close to that of Bernoulli, is obtained when taking into account the compositional heterogeneity of poly(acrylamide-*co*-acrylate)s with reactivity ratio $r_{\text{A(acrylate)}} = 0.3$ and $r_{\text{M(acrylamide)}} = 0.95$.

Figure 3. Comparison of experimental triad proportions (symbols) with those calculated for Bernoullian statistics with $P_S = F_S$ [curves, for samples (Table II)].

Reactivity ratios obtained from Kelen-Tudos plot were $r_A = 0.20$ and $r_S = 0.68$. r_A , r_S is around 0.14, indicating a tendency towards random copolymerization. A proper determination of reactivity ratios of monomers requires therefore sequence distribution analysis of copolymers with various compositions and degrees of conversion, particularly, in the low conversion range (10%), where the average copolymer composition and the instantaneous composition are similar.

The theoretical triad distribution curves match very well the experimental triad distribution curves (Figure 3). This confirms the random character of the monomer placement. The numerical values are shown in Table II. Similarly, the fraction of triads determined from C-1 and C=O group carbon resonance of the copolymer samples compares well with the theoretical values. The discrepancy in this case is quite marked and outside experimental error. This agrees with that of other authors^{5,7,18} who found that the sequence distribution of acrylamide/acrylate and acrylamide/sodium acrylate copolymers prepared by alkaline hydrolysis of PA is characterized by auto retardation kinetics and very different from Bernoullian behavior.

Error and further statistical analysis: Experimental error was not quoted above to avoid excessively complex Table II and Figure 2. F_S was obtained from the areas of the S and A signals from ^1H NMR and is therefore

determined with relatively small error of about 3% because of the clear resolution of the S and A regions. However, triad intensities are more reliable in case of *ipso* C-1 atom of styrene and less reliable in case of carbonyl group of acrylamide because of spectral overlap. Estimates of error arising from uncertainties in division of the integrals vary from 5% for the better resolved peaks of high intensity, such as AAA in sample B-91 of Figure 2, to 20% for poorly resolved or low intensity such as SAS in sample B-63 of the same Figure 2. The agreement with Bernoullian statistics is well within these limits, indicating the reactivity ratios are close to unity.

In principle, on the basis of the reactivity ratios for S/A system in other solvents one would have expected deviation from Bernoullian statistics significantly greater than the experimental errors. We thus analyzed the triad intensities in the low-conversion samples (10%) further in terms of first-order Markov statistics to compare with the Bernoullian model. The experimental and calculat-

ed values are given in Table II and Markov probabilities and reactivity ratios in Table III. The improvement in agreement of the intensities is marginal. It is found that $P_{SS} + P_{AS}$, $P_{AA} + P_{SA}$, and $P_{SA} + P_{AS} \sim 1$. Taking the experimental errors and scatter of the reactivity ratios between samples into account, we conclude in this system in case of B-30, the r_A is 0.98 ± 0.01 and $r_S = 1.04 \pm 0.01$. r_A and r_S deviate from unity in case of B-63, B-82, and B-91 samples. The monomer feed compositions do not correspond closely with the incorporation monomer composition F_S in polymer obtained by ^1H NMR spectroscopy, although these copolymers were synthesized at low conversion (<10%). However all experimental triad sequences (SSS, SSA, ASA, SAS, AAS, and AAA) match with both Bernoullian and first-order Markov statistics. In comparison, the experimental values of triad sequences are closer to Bernoullian than first-order Markov statistics.

P_{AS} decreases linearly from 0.70 to 0.29 with decrease in the concentration of styrene in copolymers while P_{SA} increases linearly from 0.29 to 0.72 with an increase in the concentration of acrylamide moieties in the copolymers. The number-average sequence lengths of S and A moieties (η_S and η_A), reciprocals of the conditional probabilities, for samples obtained using BTSAm, are calculated and shown in Tables IV(a) and (b). η_S decreases from 3.43 to 1.40 with decreasing content of styrene in the copolymers, while the values of η_A increase from 1.41 to 3.49 with increasing concentration of acrylamide in the copolymers. This shows that the number average sequence length for monomer is dependent on the concentration of that particular monomer. Number average sequence lengths appear to conform better with first-order Markovian and Bernoullian behavior. The above compositional triad distribution can be used to determine the compositions of three possible diads, *i.e.*, SS, AA, and AS using triad–diad relations.

The block character (η) is an adequate way to characterize the sequence distribution in the copolymers. It is given by the expression,¹⁹

$$\eta = [\text{SA}]/2[\text{S}][\text{A}]$$

where $[\text{SA}]$ is the mole fraction of SA diad and $[\text{S}]$, $[\text{A}]$ are the mole fractions of S and A monomers in the copolymers. The value of $0 \leq \eta < 1$ reflects more block character; $\eta = 1$ for random copolymers; the copolymer tends to alternate in the polymer structure if $1 \leq \eta < 2$. Table III shows that η for S/A copolymer obtained from BTSAm approaches 1.0, indicating that S/A copolymers have greater tendency toward random copolymerization.

The run number (R) of the copolymer is defined as the average number of the segments of either type per 100 monomer units. This may be written as²⁰

Figure 4. Theoretical triad proportions (symbols), calculated for Bernoullian statistics $P_S = F_S$ (curves), for S/A copolymers (Table II).

Table III. First order Markov addition probabilities, block character (η) and run number (R) for styrene–acrylamide Copolymers

System	P_{SA}	P_{AA}	P_{SS}	P_{AS}	P_{SA+AS}	(η)	R
B-30	0.291	0.295	0.709	0.705	0.996	0.984	41.27
B-63	0.417	0.449	0.583	0.551	0.968	0.998	49.09
B-82	0.709	0.694	0.291	0.306	1.015	0.986	42.67
B-91	0.720	0.702	0.280	0.298	1.018	0.984	40.84

Table IV(a). Number average sequence length of styrene (S) (η_S)

Copolymer designation	Observed	Calculated from	
		Bernoullian statistics	First-order Markov statistics
B-30	3.436	3.436	3.436
B-63	2.314	2.314	2.398
B-82	1.420	1.440	1.410
B-91	1.400	1.400	1.388

Table IV(b). Number average sequence length of acrylamide (A) (η_A)

Copolymer designation	Observed	Calculated from	
		Bernoullian statistics	First-order Markov statistics
B-30	1.410	1.410	1.418
B-63	1.760	1.760	1.814
B-82	3.267	3.267	3.267
B-91	3.496	3.496	3.356

Table V. Comonomer triad ratios of styrene-acrylamide copolymers

Samples	AAS/ASA		SSA/SAS	
	Observed	Calculated ^a	Observed	Calculated ^a
B-30	2.22	2.00	2.01	2.00
B-63	2.05	2.00	2.12	2.00
B-82	2.01	2.00	1.89	2.00
B-91	1.86	2.00	1.96	2.00

^a Calculated from Bernoullian statistics.

$$R = 200/(\eta_S + \eta_A)$$

where η_S and η_A are the number average sequence lengths of S and A monomer units in the copolymers shown in Tables IV(a) and IV(b). In case of S/A copolymers R lies in the range 40.84–42.67 (Table III). Table II depicts all the copolymerization parameters. Markovian triad ratios AAS/ASA and SSA/SAS are given in Table V. The examination of the triad distribution shows a good agreement with Bernoullian and first-order Markovian statistics for all polymers.

Copolymerization may result in random, or alternating copolymers, which display one single glass transition temperature, or in block or graft copolymers, which may exhibit two distinct glass transition temperatures. Depending on the structural similarity of the two monomers (*i.e.*, depending on the rotational barriers of an S–A linkage compared to either an A–A or S–S linkage), a linear relationship or positive or negative deviations from ideality can be observed. Thus, much attention has been directed theoretical models relating the glass transition to molecular structure.

Sequence length distribution of comonomers has a large influence on the chemical and physical properties of copolymers.^{21,22} The most important parameter, glass transition temperature (T_g) is affected by molecular

Table VI. Glass transition temperature (T_g) and diad composition data for styrene-acrylamide copolymers

Copolymer designation	Styrene mole fraction in feed	Diad fractions	$T_g/^\circ\text{C}$	
			Calculated from Barton's equation	Obtained from DSC
B-30	0.7	[SS]=0.50 [AA]=0.10 [AS]=0.40	137.71	138.55
B-63	0.4	[SS]=0.32 [AA]=0.19 [AS]=0.49	156.74	155.03
B-82	0.2	[SS]=0.10 [AA]=0.48 [AS]=0.42	160.56	159.80
B-91	0.1	[SS]=0.10 [AA]=0.50 [AS]=0.40	159.00	155.00

Figure 5. Plot of $T_{g,P} - N_{SS}$, $T_{g,SS} - N_{AA}$, $T_{g,AA}$ versus $N_{SA} + N_{AS}$.

weight, branching, intramolecular (triad distribution, tacticity) and intermolecular (chemical composition and molar mass distribution) copolymer microstructure.²² T_g s of all S/A copolymers (B-30 to B-91) were determined from DSC and compared with computed T_g from the diad sequence using Barton's equation²³ (Table VI).

Barton and Johnston^{23,24} described more precisely the effects of sequence distribution of monomeric unit in linear copolymers on T_g and considered the contribution of the diad. Barton's equation shows dependence on sequence as follows:

$$T_{g,P} = N_{SS}, \quad T_{g,SS} + N_{AA}, \quad T_{g,AA} + (N_{SA} + N_{AS})T_{g,SA}$$

$T_{g,P}$ is the T_g of a copolymer containing mole fraction (N) of various diads (SS, AA, SA, AS). $T_{g,SS}$ and $T_{g,AA}$ are T_g s of PS and PA respectively. $T_{g,SA}$ is T_g of the alternating copolymer and has not been reported in the literature so far. We thus calculated $T_{g,SA}$ using experimental $T_{g,P}$ from DSC of S/A copolymers in above equation and plotting ($T_{g,P} - N_{SS}$, $T_{g,SS} - N_{AA}$, $T_{g,AA}$) against ($N_{SA} + N_{AS}$). The plot gives a straight line with zero intercept with slope 91.63°C (Figure 5). $T_{g,SA}$ calculated from slope was thus 91.63°C which was used

Figure 6. Variation of $T_{g,p}$ and sequence length (η_A) with acrylamide incorporation (mol%) in the S/A copolymers.

for further calculation of $T_{g,p}$ from Barton's equation in Table VI. T_g s for PS and PA were 100 and 155.56°C, respectively. T_g obtained from diad concentrations were in good agreement with values obtained from DSC (Table VI).

Experimental $T_{g,p}$ are plotted against mol% acrylamide incorporation in copolymer and sequence lengths (Figure 6). $T_{g,p}$ increases linearly upto 45 mol% acrylamide and the curve levels off as it approaches the value for PA homopolymer (155.56°C). Apparently the free volume required for the segmental motion increases rapidly as the copolymer composition approaches 45% of acrylamide. Above this composition, additional free volume required for segmental motion is small.

For copolymers, obtained (Table VI) T_g increases and becomes steady with increasing A-A diad concentration. Similarly, T_g decreases rapidly from B-91 to B-63. This direct dependence of T_g on diad concentration explains the agreement between measured and predicted T_g . Harris *et al.*²² observed similar behavior in acrylonitrile-4-vinylpyridine copolymer system. Johnston's method of predicting T_g value²⁴ assumes that T_g of copolymer can be based on the components representing the T_g s of the various linkages (S-S, A-S, A-A) within the copolymers. Clearly there is a correlation between the T_g and the monomer sequence distribution for S/A copolymers. Average sequence length η_A increases with T_g (Figure 6).

CONCLUSION

The sequence distribution at triad level for poly(styrene-co-acrylamide) obtained from ^{13}C NMR matches better Bernoullian statistics. The product of the reactivity ratio r_A and r_S calculated using ^{13}C NMR approaches unity indicating the random nature of the copolymers. The number average sequence length of either monomer (S, A) calculated from diad and triad sequence is dependent on the concentration of that particular monomer. The block character further confirms random

copolymerization. The glass transition temperatures of the copolymers were theoretically estimated from diad sequence and compared with experimental $T_{g,p}$ obtained from DSC. Agreement was found between the two T_g obtained from DSC. The agreement between the two T_g was consistent. The diad sequence made possible calculation of $T_{g,SA}$ of alternating copolymers.

Thus, a use of a protected acrylamide, namely, *N,O*-bis(trimethylsilyl)acrylamide, made possible solution copolymerization with styrene to yield, after deprotection, a truly random copolymer of styrene and acrylamide. This hitherto has not been possible primarily due to different solubility characteristics of the two monomers.

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REFERENCES

1. S. I. Kuchanov, *Adv. Polym. Sci.*, **103**, 1 (1992).
2. A. Dasgupta and S. Sivaram, *Macromolecules*, **27**, 1665 (1994).
3. A. Dasgupta and S. Sivaram, *Macromol. Chem. Phys.*, **195**, 3361 (1994).
4. F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," 2nd ed, Academic Press, New York, N.Y., 1987.
5. N. D. Truong, J. Francois, J. C. Galin, and Q. T. Pham, *Polymer*, **27**, 459 (1986).
6. N. D. Truong, J. C. Galin, J. Francois, and Q. T. Pham, *Polymer*, **27**, 467 (1986).
7. F. Candau, Z. Zekhnini, and F. Heatley, *Macromolecules*, **19**, 1895 (1986).
8. A. Staubli, E. Mathiowitz, and R. Langer, *Macromolecules*, **24**, 2291 (1991).
9. G. H. J. Van Doremale, A. L. German, N. K. De Vries, and G. P. M. van der Velden, *Macromolecules*, **23**, 4206 (1990).
10. D. J. T. Hill, L. Dong, and J. H. O'Donnel, *J. Polym. Sci., Polym. Chem.*, **31**, 2951 (1993).
11. J. C. Randall, Jr., "Polymer Sequence Determination: Carbon-13 NMR Method," Academic Press, London, 1997, Chapter 4.
12. G. Odian, "Principles of Polymerization," Wiley, New York, N.Y., 1981, pp 425-433.
13. N. D. Truong, J. C. Galin, J. Francois, and Q. T. Pham, *Polym. Commun.*, **24**, 208 (1984).
14. J. F. Lancaster and M. N. O'Connor, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 547 (1982).
15. Y. Inoue, T. Fukutomi, and R. Chûjô, *Polym. J.*, **15**, 103 (1983).
16. M. F. Llauro, C. Pichot, J. Guillot, G. L. Rios, M. A. Cruz, and C. Guzman, *Polymer*, **27**, 889 (1986).
17. Y. Inoue, A. Nishioka, and R. Chûjô, *Makromol.*, **156**, 207 (1972).
18. F. Halverson, J. E. Lancaster, and M. N. O'Connor, *Macromolecules*, **18**, 1139 (1985).
19. K. Ito and Y. Yamashita, *J. Polym. Sci., Part A*, **3**, 2165 (1965).
20. H. R. Allock and F. W. Lampe, "Contemporary Polymer Chemistry," Englewood Cliff, New Jersey, 1990, Chapter 12/II, p 116.
21. F. Arranz, M. Sanchez-Chaves, and A. Molinero, *Makromol. Chem.*, **185**, 2153 (1984).
22. S. H. Harris and R. D. Gilbert, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1653 (1982).
23. J. M. Barton, *J. Polym. Sci., Part C*, **30**, 573 (1970).
24. N. W. Johnston, *J. Macromol. Sci., Rev. Macromol. Chem.*, **14**, 215 (1976).