Microstructure determination of styrene-acrylonitrile copolymers by $^{13}$C NMR spectroscopy

A S Brar*, G S Kapur & M S Sekhar
Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110 016
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Styrene-acrylonitrile (S-A) copolymers having different proportions of the monomers have been bulk copolymerised at 70°C, using benzoylperoxide as the initiator. The reactivity ratios have been calculated using the Kelen-Tudos method. A detailed study of the microstructure of the copolymers has been carried out using $^{13}$C NMR spectroscopy. The experimental styrene-and acrylonitrile-centered triad sequence distributions have been determined by using aromatic (C$_1$) carbon and nitrile (C-N) carbon resonances, respectively. These results are found to be in good agreement with those calculated theoretically using reactivity ratios [Harwood H J, J polym Sci, 25 (1968) 37].

The styrene-acrylonitrile copolymers are of increasing commercial importance. These resins have an excellent balance of physical and chemical properties. The solution, bulk, and chemical properties of the copolymers depend on their microstructure. Hill et al. have reviewed the mechanism of copolymerisation of styrene and acrylonitrile using various models. They have also explained the significant consequences of these models with respect to the mode of copolymerisation. Guyot and Guillot have reported the necessity to introduce penultimate and antepenultimate effects for the copolymerisation of this system.

Recently, several studies have proved the usefulness of $^{13}$C NMR for the examination of cotacticity and sequence distributions of various copolymers.

In our earlier publications, the sequence distributions of copolymers of methyl methacrylate with ethyl methacrylate, acrylic acid, styrene, n-butyl methacrylate, and acrylonitrile-ethyl methacrylate copolymers have been reported. Literature survey reveals that previous work on styrene-acrylonitrile copolymers is confined to the triad sequence determination by NMR spectroscopy, but no tetrad and pentad sequence distributions have been reported for this copolymer system based on theoretical models using reactivity ratio values. Therefore, in this paper we report the sequence distribution of styrene-acrylonitrile copolymers using $^{13}$C NMR spectroscopy and terminal reactivity ratios based on Harwood’s computer program. Excellent agreement between the experimental and theoretical sequence distributions allowed us to calculate higher-ad sequence distribution up to pentad using Harwood’s program.

Materials and Methods

Synthesis of copolymers

Acrylonitrile (A) and styrene (S) were purified by vacuum distillation, followed by washing with 5% NaOH. The monomers were then washed repeatedly with water and dried over anhydrous sodium sulphate.

Styrene-acrylonitrile copolymers having different proportions of monomer were prepared using benzoylperoxide as the initiator at 70°C. The copolymerisation was stopped at a conversion of less than 5% by precipitation into excess of petroleum ether. The samples were vacuum-dried, and used for further analysis.

Determination of copolymer compositions and molecular weights

The C, H, and N contents of the copolymers were determined using a Perkin Elmer 240 C elemental analyzer. From the %N values, the copolymer compositions were calculated. The change in copolymer composition ($F_t$) with monomer composition in feed ($f_t$) is shown in Fig. 1. The molecular weights were determined by viscometry at 30 ± 0.1°C in butanone using the Mark-Houwink equation:

\[ [\eta] = 0.36 \left[ M \right]^{0.61} \]

where [\eta] is the intrinsic viscosity and \( M \) is the molecular weight. The copolymer compositions and molecular weights are listed in Table 1.

NMR analysis

Both $^1$H and $^{13}$C NMR spectra were recorded on a Jeol FX100 NMR spectrometer. The operating frequencies were 100 and 25 MHz respectively. For copol-
Table 1—Copolymerisation data for styrene-acrylonitrile system

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feed in composition (mol %)</th>
<th>% N in copolymer</th>
<th>Copolymer composition (mol %)</th>
<th>Intrinsic viscosity [η], dl/g</th>
<th>Mol. wt. × 10^-5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AN</td>
<td>ST</td>
<td></td>
<td>AN</td>
<td>ST</td>
</tr>
<tr>
<td>A</td>
<td>20</td>
<td>80</td>
<td>3.04</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>B</td>
<td>23</td>
<td>77</td>
<td>3.32</td>
<td>22</td>
<td>78</td>
</tr>
<tr>
<td>C</td>
<td>30</td>
<td>70</td>
<td>3.61</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>D</td>
<td>43</td>
<td>57</td>
<td>5.00</td>
<td>32</td>
<td>68</td>
</tr>
<tr>
<td>E</td>
<td>65</td>
<td>35</td>
<td>8.14</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td>F</td>
<td>77</td>
<td>23</td>
<td>8.71</td>
<td>49</td>
<td>51</td>
</tr>
<tr>
<td>G</td>
<td>93</td>
<td>7</td>
<td>12.68</td>
<td>64</td>
<td>36</td>
</tr>
<tr>
<td>H</td>
<td>97</td>
<td>3</td>
<td>14.60</td>
<td>71</td>
<td>29</td>
</tr>
</tbody>
</table>

Fig. 1  Copolymer composition (mol % F1) as a function of feed in monomer composition (mol % f1) [(---) theoretical behaviour and (o---) experimental points]

Results and Discussion

Determination of reactivity ratios

The Kelen-Tudós18 method was used for the calculation of reactivity ratios. The terminal model reactivity ratios obtained were: rA = 0.055 and rS = 0.85. Since the product of rA and rS is very much less than 1(0.047), the system follows random distribution of monomer units.

1H NMR studies

For polyacrylonitrile, the methine (CH) protons are observed at δ3.1 ppm, and methylene(CH2) protons at δ2.08 ppm. The downfield absorption of methine compared to methylene protons is due to the presence of contiguous nitrile groups. The wide range of absorption of these protons indicates their sensitivity to stereo-chemical changes, and spin-spin coupling in the system.

The 1H NMR spectrum of polystyrene shows absorption in three different regions. The absorption in the range δ1.75-2.00 ppm is due to methine protons, and the band between δ1.20 and 1.71 ppm is due to methylene protons. The aromatic protons resonate as two different peaks: one centered at δ6.60 ppm which is attributed to ortho-protons, and the other, a multiplet, in the range δ7.0-7.5 ppm due to meta- and para-protons. The broadness of peaks is due to their susceptibility to stereochemical changes, steric effects, and spin-spin coupling effects.

Figure 2 shows the 1H NMR spectra of styrene-acrylonitrile copolymers of different compositions. The assignments of 1H NMR spectra for copolymers are based on the observed changes in the peak position with change in composition of copolymer and comparison with homopolymer spectra. It was observed that with the increase in concentration of styrene in copolymers, the peak at δ3.00 ppm in sample F (51 mol % S) shifted to δ2.55 ppm in sample D (68 mol % S) and to δ2.48 ppm in sample B (78 mol % S). This upfield shift with consequent decrease in intensity is due to the shielding effect of S units on A units. This peak is assigned to methine protons of A unit in copolymer. In sample B (78 mol % S), the two aromatic peaks are shifted downfield to δ6.68 ppm (o) and 6.71 ppm (m & p) respectively. With a decrease in concent-
Fig. 2—$^1$H NMR spectra for styrene-acrylonitrile copolymers [(a) B (S mol % 78); (b) D (S mol % 68) and (c) F (S mol % 51)].

...ration of S units in copolymer in sample D (68 mol % S) these two peaks merge to a shoulder at δ6.94 ppm and δ7.20 ppm. On further decrease in concentration of S in sample F (51 mol % S), only a singlet at δ7.35 ppm is observed. Thus, an increase in concentration of A in copolymers provides a deshielding effect to the aromatic peaks of S units.

The broad peak centered at δ1.65 ppm is attributed to the overlapping absorption of methylene and methine protons of S units as well as methylene protons of A units. As the peaks were very poorly resolved, sequence determination using the $^1$H NMR spectroscopy was not possible.

$^{13}$C NMR studies

The $^{13}$C NMR spectrum of polyacrylonitrile showed a triplet at δ120.06, 119.86 and 119.76 ppm due to nitrile carbons in A unit. It is sensitive to tacticity differences (mm,mr/rm and rr respectively) in the polymer backbone. Two sharp peaks at δ37.01 ppm and δ27.7 ppm were observed. They are assigned to methylene and methine carbons of the polymer respectively. Polystyrene also showed absorption in three different regions. The most downfield absorption is observed between δ145 and 146 ppm. The expanded region showed a triplet at δ145.26, 145.60 and 146.00 ppm which was assigned unambiguously to aromatic C1 carbon of phenyl ring. The triplets are assigned as mm, mr/rm and rr sequences in the polymer respectively. Two moderately broad peaks centered at δ127.87 and δ125.53 ppm were observed. These two resonances are attributed to C2,3,5 & 6, and C1 carbons of phenyl ring respectively. The broad peak in the region between δ46.4 and δ42.4 ppm has been assigned to the overlapping methylene and methine carbons.

$^{13}$C{$^1$H} NMR spectrum of copolymer F (49 mol % A) is shown in Fig. 3. The aromatic C1 carbon triplet is shifted upfield to δ142.2, 141.8 and 140.3 ppm. This triplet was assigned to the differences in triad comonomer placements as SSS, SSA/ASS and ASA respectively. Further fine-structure in these triplets was observed which could be due to their sensitivity to higherad comonomer sequences or to stereocchemical changes in the copolymer. In the copolymer, the nitrile carbon (of A unit) absorption shifted downfield. Two peaks were observed at δ120.9 and δ120.2 ppm. A very small peak was observed at δ120.00 ppm. These three peaks are assigned as SAS, SAA/AAS and AAA sequences respectively. The intensity of SAS peak was high even at low concentrations of A in copolymer while the intensity of AAA peak was very small even at a high concentration of A in copolymer.
Determination of comonomer sequence distribution

The nitrile carbon signal was used to calculate concentration of A-centered triad sequences and the phenyl C_1 carbon signal was used to calculate the concentration of S-centered triad sequences in the copolymer. The expanded regions of aromatic C_1 carbon of S unit, and nitrile carbon region of A unit in copolymer were considered for the calculation of comonomer centered triad fractions. All the triplets exhibited fine structure due to their sensitivity to higher-ad comonomer sequences and stereochemical changes with copolymer composition.

Table 2—Comparison of A-centered triad sequence fractions
[a - from ^13^C NMR, b - Harwood program]

<table>
<thead>
<tr>
<th>Sample</th>
<th>AAA</th>
<th>AAS+SAA</th>
<th>SAS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>a</td>
</tr>
<tr>
<td>E</td>
<td>0.01</td>
<td>0.01</td>
<td>0.15</td>
</tr>
<tr>
<td>G</td>
<td>0.22</td>
<td>0.18</td>
<td>0.45</td>
</tr>
<tr>
<td>H</td>
<td>0.39</td>
<td>0.41</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 3—Comparison of S-centered triad sequence fractions
[a-from ^13^C NMR, b-Harwood program]

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSS</th>
<th>SSSA+ASS</th>
<th>ASA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>a</td>
</tr>
<tr>
<td>B</td>
<td>0.45</td>
<td>0.55</td>
<td>0.43</td>
</tr>
<tr>
<td>C</td>
<td>0.44</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>D</td>
<td>0.32</td>
<td>0.28</td>
<td>0.43</td>
</tr>
<tr>
<td>E</td>
<td>0.21</td>
<td>0.10</td>
<td>0.40</td>
</tr>
<tr>
<td>F</td>
<td>0.19</td>
<td>0.04</td>
<td>0.26</td>
</tr>
</tbody>
</table>

This observation could be corroborated from the large differences in reactivity ratios ($r_A = 0.055$ and $r_S = 0.85$); the A unit in the polymer chain always prefers to add on to S unit during copolymerization.

The peaks due to aromatic C_4 carbon and other carbons (2,3,5 and 6) were observed at $\delta$125.53 and $\delta$127.2 ppm respectively. There were very little changes in peak positions of these carbon resonances with copolymer composition. A broad band observed between $\delta$37.2 and 41.1 ppm was assigned to the overlapping of methylene and methine carbons of S, and methylene carbon of A units. The methine carbon of A unit gave a peak at $\delta$27.2 ppm.

Fig. 3—25 MHz $^13^C$/$^1^H$ NMR spectra for styrene-acrylonitrile polymers: F (AN mol % 49); G (AN mol % 64) and H (AN mol % 71).

Fig. 4—Normalized statistical monomer triad sequence distribution versus acrylonitrile (mol %) in styrene-acrylonitrile CO polymers [—O—] theoretical distribution and (x) experimental distribution.

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hin a particular triad sequence. Theoretically, we have calculated the concentration of A- and S-centered triad sequences in each copolymer by Harwood’s program using terminal reactivity ratios ($r_A = 0.055; r_S = 0.85$). The input data for Harwood’s program consisted of monomer reactivity ratios, the composition of the feed, the molecular weights of the comonomers and the percentage conversion. The changes in these triad sequences with increase in concentration of acrylonitrile are shown in Fig. 4.

These theoretical values were compared with experimental values calculated from NMR spectra (Tables 2 and 3). A good agreement between the experimental and theoretical distribution indicates that kinetics of styrene-acrylonitrile copolymerization can be explained satisfactorily using the terminal model. This good agreement indicates that Harwood’s program can be used to predict the theoretical values for higher-ad sequences. The fractions of higher-ad sequences are given in Tables 4 and 5.

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**References**

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