Styrene/acrylonitrile alternating copolymers

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Alternating copolymers of styrene (S) and acrylontrile (AN) are produced preferentially when S and AN are copolymerized at temperatures below 60°C. The tendency for alternation decreases at higher temperatures. Excess S produced block copolymers at a slower rate than the S/AN copolymers.

INTRODUCTION

It has been previously reported that normally alternating copolymer systems of styrene/maleic anhydride (S/MA) and α-methylstyrene/MA (α-MS/MA) yield random copolymers when the copolymerizations are carried out at elevated temperatures[1,2]. Thus the S/MA and the α-MS/MA systems yield random copolymers at temperatures above 120° and 90°C, respectively. The alternation of the units in the copolymers has been attributed to a mechanism involving charge transfer complexes (*CTC*) as the polymerizable species[3]. This mechanism is supported because of the existence of the *CTC* in solutions of the monomer pairs as shown by both n.m.r. and u.v. spectrophotometry[4,5].

A more complicated *CTC* involves the use of metal salts acting as Lewis acids. Examples of these salts are zinc chloride ($ZnCl_2$)[6,7], ethyl aluminium sesquichloride (EASC)[8], and magnesium and nickle chloride[9]. These salts polarize the electron acceptor which then allows it to form a *CTC* with an electron donor. This three molecule entity is then the polymerizable species[10]. It has been reported that the styrene/acrylonitrile–zinc chloride, (S/AN)–$ZnCl_2$, system also yields highly alternating copolymers[11] but that the (S/AN)–EASC system yields random copolymers when polymerized at 70°C[12].

The (S/AN)–$ZnCl_2$ system has been shown to have absorbance bands in the u.v. region attributed to a *CTC* which is not characteristic of either monomer species[13]. It is believed that the high degree of alternation of the units in the copolymer prepared at low temperature is due to the *CTC*, while the more random sequencing of units in the copolymer prepared at elevated temperatures is caused by the disappearance of the *CTC* at higher temperatures.

The effect of composition of the reactants (S/AN)–$ZnCl_2$, solvent and temperature on the rate of polymerization and composition of the copolymer has been investigated in this study. The (S/AN)–$ZnCl_2$ complex was detected by u.v. and ^1H n.m.r. techniques. The polymerization rates were monitored by dilatometry and the solvent fractionated products were characterized by pyrolsis gas chromatography (p.g.c.), ^{13}C n.m.r. and differential scanning calorimetry (d.s.c.).

EXPERIMENTAL

Reagent grade t-butanol (t-BuOH) was dried over molecular sieves. The monomers were distilled under reduced pressure and stored at 0°C until used. Reagent grade zinc chloride was used as received. t-Butyl peroxpivalate (t-BPP) as a 75% solution in mineral spirits with a half-life of 12 h at 50°C was used as the initiator.

^1H n.m.r. spectra were obtained on a Varian Model T-60 instrument using tetramethylsilane as an internal standard. The spectra of the monomers were obtained on neat solutions. Spectra of samples containing $ZnCl_2$ were obtained by dissolving $ZnCl_2$ in AN followed by the addition of S when desired. The u.v. absorbance data were obtained with a Carey Model 14 Scanning Spectrophotometer using t-butanol as the solvent. Monomer concentration was 10^{-3} M in all solutions. The concentration of $ZnCl_2$ was 10^{-4} M.

High resolution proton noise decoupled ^{13}C n.m.r. spectra were obtained with a Varian XL-100-15 spectrometer and Nicolet Technology TT-100 Data System in the Fourier transform mode. The pulse time was 100 msec and the acquisition time was 1 sec. Spectra were recorded in deuterodimethyl suphoxide using an 8K data table and a 6KH^2 sweep width. Differential scanning calorimetry (d.s.c.) data were collected with a Du Pont Model 990 thermal analyser equipped with a d.s.c. cell. All runs were made in a N_2 atmosphere over a temperature range of 0° to 350°C.

The rate data were obtained by use of the Seymour–Stahl recording capacitance dilatometer[14]. The samples were polymerized in the dilatometer at 50°C.

Equimolar amounts of S and AN (0.020 M) were copolymerized with and without a 10 mol % ratio of $ZnCl_2$ (0.002 M) in 20 ml of t-BuOH with 2.5% t-BPP as the initiator. The reaction was carried out at 50°C in 1 fl oz amber bottles for 96 h. Further copolymerizations of S, AN, and $ZnCl_2$ in

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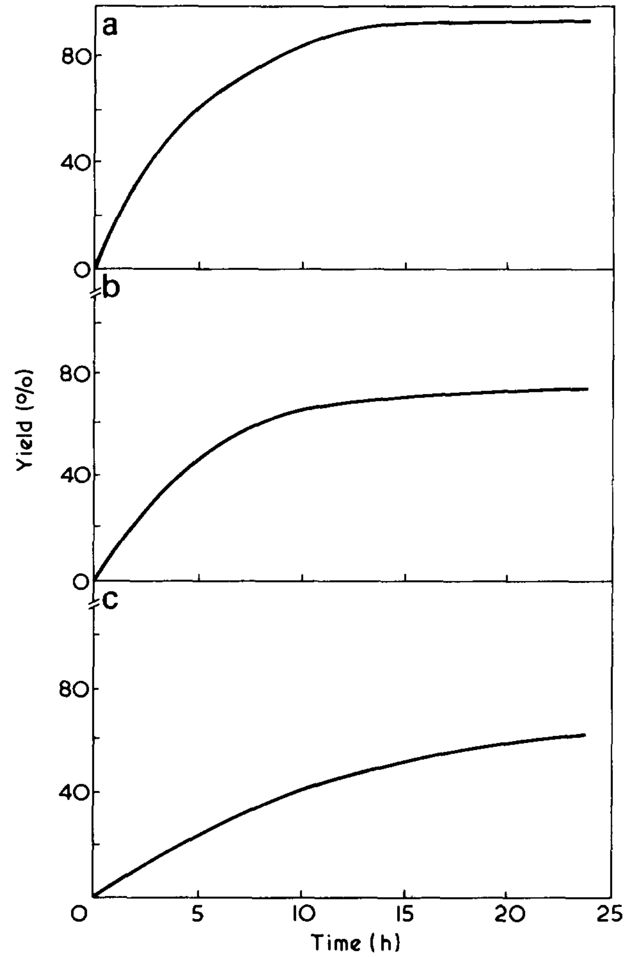

Figure 1 Copolymerization rates of styrene: acrylonitrile at (a) 1:1; (b) 2:1; (c) 4:1

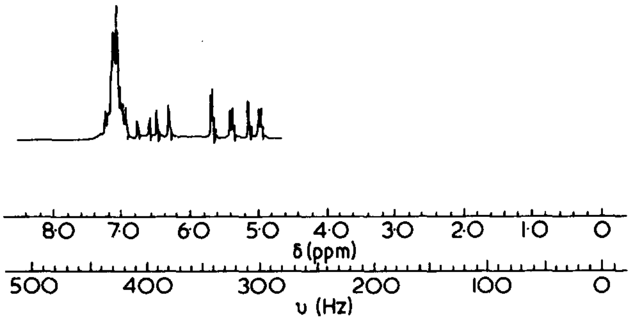

Figure 2 Proton nuclear magnetic resonance spectrum of styrene

the ratio 5:10:1 (0.20 M:0.40 M:0.04 M), respectively, were carried out in 200 ml t-BuOH with 2.5% t-BPP as the initiator. These reactions were carried out at 50° and 70°C in ½ pt amber glass bottles for a period of 4 h. The products were characterized by p.g.c., d.s.c., and ^{13}C n.m.r.

As shown in *Figures 1a–1c*, abrupt changes in the copolymerization rates of S and AN were noted when the available AN was consumed in the formation of the alternating S/AN copolymer. When excess S was present, the rate of S block formation was slower than that of the alternating S/AN copolymer as shown in *Figure 1a* and the initial copolymerization in *Figure 1b* (2:1 ratio S:AN) and *Figure 1c* (4:1 ratio S:AN), respectively. Excess S produces a block copolymer of the form poly(styrene-co-acrylonitrile-*b*-styrene), P(S/AN–S). The fact that styrene blocks could be produced under these conditions has been previously suggested[15].

Evidence for the *CTC* between S and AN–ZnCl$_2$ has been demonstrated by ^1H n.m.r. The centre of the AN vinylic proton absorbance is at 5.90 δ. When ZnCl$_2$ is present in a 0.10 mole ratio the centre of the absorbance shifts downfield to 6.00 δ. This corresponds to removal of electrons from AN, making the monomer more electron deficient. Upon the addition of S(S:AN:ZnCl$_2$, 10:10:1) the centre of the AN absorbance shifts upfield to 5.60 δ. This corresponds to a donation of electrons from S to the AN–ZnCl$_2$ complex resulting in a three membered complex with electron density flow given by: $S \rightarrow AN \rightarrow ZnCl_2$. The S vinylic peaks are also observed to shift downfield approximately 0.1 δ each. *Figures 2* and *3* show the n.m.r. spectra of S and AN, respectively, while *Figure 4* shows the effect of ZnCl$_2$ on AN at the 10:1 ratio. *Figure 5* shows the ^1H n.m.r. spectra of the

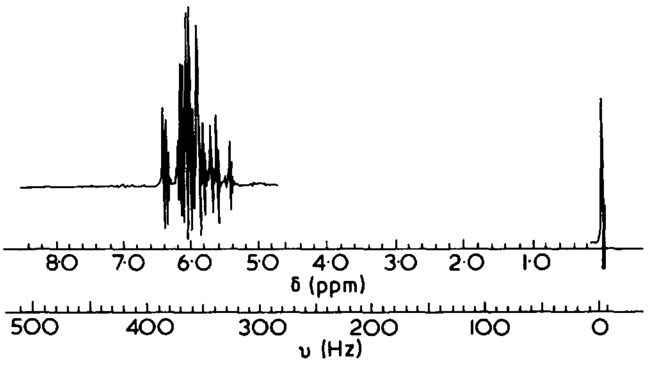

Figure 3 Proton nuclear magnetic resonance spectrum of acrylonitrile

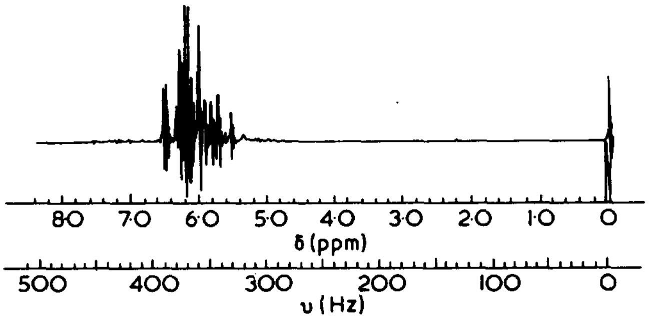

Figure 4 Proton nuclear magnetic resonance spectrum of acrylonitrile complexed with zinc chloride in a 10:1 ratio

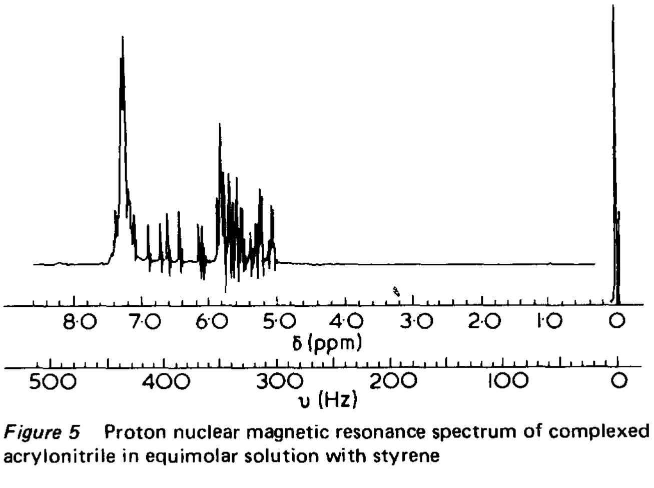

Figure 5 Proton nuclear magnetic resonance spectrum of complexed acrylonitrile in equimolar solution with styrene

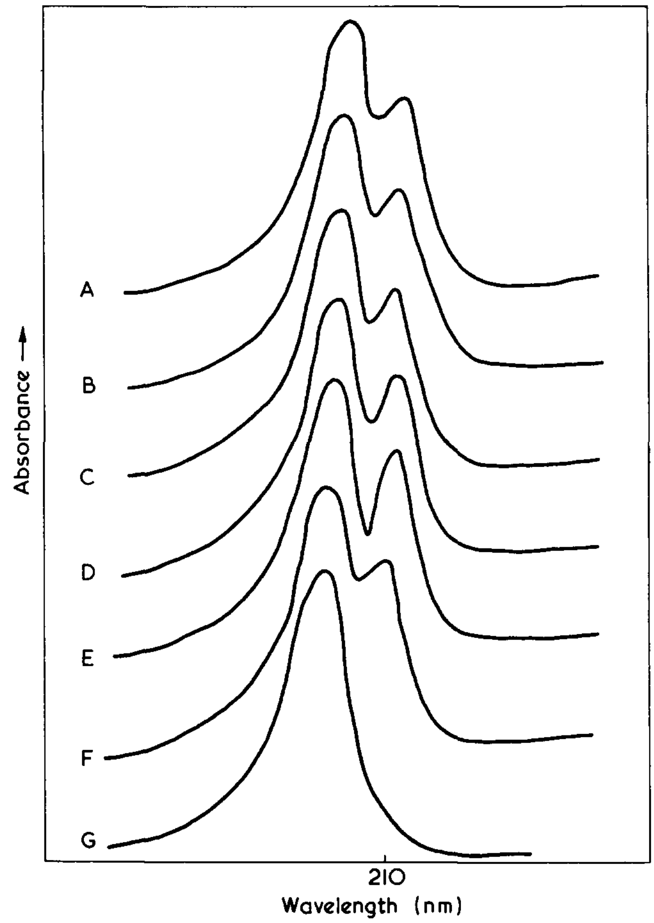

Figure 6 Ultra-violet spectra of styrene/acrylonitrile zinc chloride at 60°C (A); 55°C (B); 50°C (C); 40°C (D); 30°C (E); acrylonitrile at 30°C (G) and styrene/acrylonitrile at 30°C (F)

CTC of S, AN, and $ZnCl_2$. The effect of temperature on the *CTC* was investigated by u.v. spectrophotometry.

The u.v. absorbance shown in *Figure 6* are somewhat atypical. Generally, the absorbance bands due to the *CTC* manifest themselves as shoulders on already existing absorbances. In the S/AN–$ZnCl_2$ system there is a new absorbance band at 214 nm due to the interaction of S and AN that is enhanced by the addition of $ZnCl_2$. It was previously shown that S and AN had reactivity ratios of 0.40 and 0.04, respectively[16], and thus the possibility of precopolymerization interaction was indicated. Upon increasing the temperature, the absorbance decreased until the temperature reached 60°C. This temperature was designated as the ceiling temperature for the S, AN and $ZnCl_2$ CTC. In order to establish the effect of the *CTC* on the copolymerization of S and AN–$ZnCl_2$, copolymerizations were carried out at temperatures below and above the 60°C ceiling temperature as determined by u.v. methods.

CHARACTERIZATION OF COPOLYMERS

The reactivity ratios for S and AN in the S/AN 1:1 systems are 0.40 and 0.04, respectively[16]. A strict alternation of units is not followed, but for equimolar copolymerizations, a certain degree of alternation is observed. Thus, the copolymers produced at 50°C with and without $ZnCl_2$ should have the greatest differences in composition. Yet, a comparison of p.g.c. pyrograms for these copolymers showed only approximately 10% difference in the characteristic peak areas. Therefore, establishing the existence of an alternating mechanism requires information concerning the sequencing of units and not the relative ratio of units in the copolymer.

Figure 7 shows the ^{13}C n.m.r. absorbance of the nitrile and phenyl nuclei of S/AN copolymer prepared from an AN:S ratio of 2:1 in the presence of $ZnCl_2$ at 70°C. The nitrile carbon nucleus is split into a triad with the left-most absorbance representing S–$\underline{\text{AN}}$–S, the right-most peak representing AN–$\underline{\text{AN}}$–AN–, and the centre absorbance representing –AN–$\underline{\text{AN}}$–S– or –S–$\underline{\text{AN}}$–AN–[17]. Since the copolymer was prepared at a temperature greater than the ceiling temperature of 60°C, it is not surprising that the absorbance indicating an alternation of units is quite small, while the absorbances due to non-alternating sequences are large. *Figure 8* shows the ^{13}C n.m.r. absorbance of the nitrile and phenyl carbon nuclei of S/AN copolymer prepared from an AN:S ratio of 2:1 in the presence of $ZnCl_2$ at 50°C. Comparison of the two spectra clearly indicates an increase in alternation for the copolymer prepared at 50°C.

Differences in physical properties of the copolymer are shown by d.s.c. thermograms of the copolymers. (*Figure 9a* shows a null thermogram giving characteristic instrumental artefacts.) Unfortunately, artefacts of the instrument occur at approximately the same temperature as the glass transition temperatures for both polystyrene (100°C)[17] and polyacrylonitrile (97°C)[18].

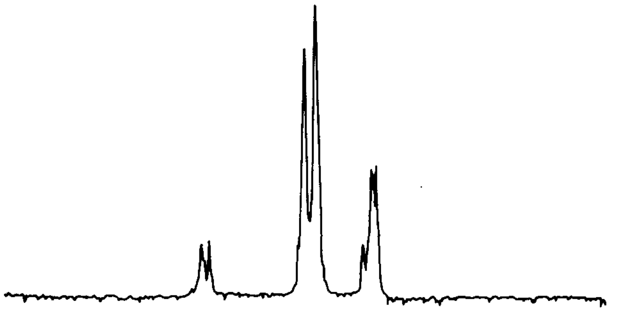

Figure 7 ^{13}C nuclear magnetic resonance spectrum of the nitrile carbon of a copolymer prepared from the styrene/acrylonitrile–zinc chloride at 70°C

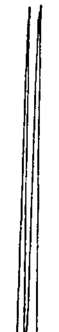

Figure 8 ^{13}C nuclear magnetic resonance spectrum of the nitrile carbon of a copolymer prepared from the styrene/acrylonitrile–zinc chloride system at 50°C

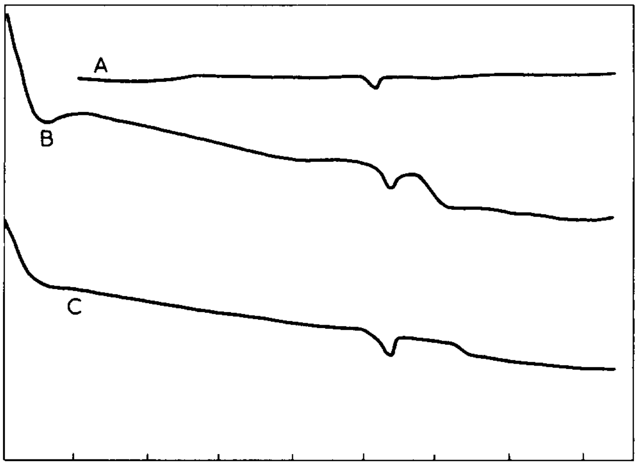

Figure 9 A, null differential scanning calorimetry thermogram, B, (S/AN) highly alternating; C, (S/AN) random

The d.s.c. thermogram for the S/AN copolymer prepared at 50°C is shown in *Figure 9b*. A glass transition temperature of 115°C is noted. The d.s.c. thermogram for the S/AN copolymer produced at 70°C is shown in *Figure 9c*. Here, the glass transition temperature is raised to 120°C clearly indicating changes in the copolymer composition.

From an analysis of d.s.c. data for the S/AN induced alternating system, there are shown to be changes in the copolymer composition for the system prepared at 50° and 70°C. The ^{13}C n.m.r. data indicate that a greater degree of alternation is present in the copolymer prepared below the 60°C ceiling temperature as determined by u.v. spectrophotometry. The authors believe that the greater degree of alternating sequences in the copolymer is due to the polymerization of the *CTC* at temperatures below 60°C.

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