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Donor-Acceptor Complexes in Copolymerization. XVII. NMR Analyses of Random and Alternating Styrene— α-Chloroacrylonitrile Copolymers

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SUMMARY

The NMR spectra of random and equimolar alternating copolymers of styrene with α-chloroacrylonitrile were studied. The monomer sequence distribution in the random copolymers, prepared in the presence of free radical catalysts, as determined from NMR analyses, was in accordance with the values expected from the r_1 and r_2 values derived from the conventional copolymerization theory. The alternating structure of the copolymer prepared by complexation with $AlEt_{1.5}Cl_{1.5}$ was confirmed. The equimolar random copolymer, prepared by free radical initiation, was shown to contain essentially alternating sequences.

INTRODUCTION

NMR studies have made it possible to determine the microstructure in copolymers including comonomer sequence distribution and cotactic configurations [1-4]. This has been especially possible in copolymers containing aromatic units because of the large chemical shift associated with the diamagnetic shielding provided by the aromatic ring. NMR has thus provided a means to distinguish between random and alternating copolymers and gives evidence of the presence of alternating sequences in random copolymers [5, 6].

The present investigation relates to the NMR spectra of styrene–α-chloroacrylonitrile (S-CA) copolymers. The reactivity ratios for α-chloroacrylonitrile (r_1) and styrene (r_2) in this system are reported to be $r_1 = 0.13$, $r_2 = 0.06$ at 60°C [7] and $r_1 = 0.08$, $r_2 = 0.10$ at 80°C [8]. The low values for the reactivity ratios suggest a strong alternating tendency for the monomeric units in copolymers obtained at low conversions, i.e., the sequences CA-S-CA and S-CA-S would be predominant as compared to other sequences, particularly in copolymers having equimolar monomeric compositions. In other words, the copolymers analyzing as equimolar comonomer compositions would have essentially alternating sequences irrespective of the method of preparation. Since it is possible to prepare the alternating copolymer via metal halide complexation, its NMR spectrum should demonstrate the presence of the alternating sequence in the various random copolymers prepared by conventional free radical initiation.

EXPERIMENTAL

Random Copolymers

The random copolymers were prepared in bulk at 60°C using azobisisobutyronitrile as the initiator. The polymerization mixtures were poured into methanol to precipitate the polymers. The copolymers were purified by solution in acetone and precipitation in methanol and were dried in vacuo at 40°C.

Alternating Copolymer

The 1:1 alternating copolymer was prepared by a method similar to that used in the preparation of various alternating copolymers. Styrene and α-chloroacrylonitrile were placed in a reaction flask fitted with a self-sealing rubber cap, thermometer, stirrer, and nitrogen inlet and outlet. The mixture was maintained under nitrogen and stirring at 25°C in a thermostated bath. A toluene solution of ethyl aluminum sesquichloride was introduced slowly through a hypodermic syringe. The reaction mixture thickened in a few minutes and the reaction was terminated at low conversion by the addition of methanol. The product was purified by solution in a mixture of acetone and benzene and precipitation into methanol. The product was found to be a mixture of the equimolar alternating copolymer and polystyrene or a high styrene content copolymer. The mixture was separated by extraction in a Soxhlet extractor with cyclohexane which removed the high styrene content copolymer. The residue was the alternating copolymer which was dissolved in acetone and precipitated in methanol. The product was dried in vacuo at 40°C.

The alternating copolymer could be prepared in the presence of anhydrous zinc chloride. The alternating copolymer was always accompanied by the high styrene content copolymer where the weight fraction of the latter was dependent on the mole ratio of the monomers in the feed, temperature, concentration of the metal halide, and presence of radical catalysts. The formation of the latter could be avoided by carrying out the copolymerization in solvents such as DMF and DMSO.

NMR Measurements

The NMR spectra of the free radical initiated random copolymers were examined in $CDCl_3$ or deuterated acetone (acetone-d_6) at 70°C and the alternating copolymers in $CDCl_3$ at 73°C at 100 MHz using tetramethylsilane as the internal standard.

RESULTS AND DISCUSSION

Figure 1 presents the NMR spectrum of the 1:1 alternating styrene–α-chloroacrylonitrile (S-CA) copolymer prepared by complexation with $AlEt_{1.5}Cl_{1.5}$. The spectrum is simple and shows three principal areas of sharp absorption. The aromatic ring protons appear as two peaks centered at 2.75 and 2.92 τ. The splitting in the phenyl resonance should not be considered as mainly due to the diamagnetic shift of the ortho protons arising from successive styrene units. It is generally understood that this is also due to other environmental groups. Similar splitting of aromatic portions is also known to be present in alternating copolymers of acrylonitrile with styrene [5] and α-methylstyrene [6] and styrene–methyl acrylate [9] copolymers.

The α-methine proton of the styrene unit appears as a single peak centered at 6.62 τ. This assignment is based on the relative peak area measurements. It is significant that the methine proton resonance has shifted so far downfield, and this can be attributed to the strong electronegativity of the adjacent α-chloroacrylonitrile (e = +1.40) unit. Since the methine proton appears as a single peak and no multiplicity is observed, it is not possible to determine the extent of cotactic configurations.

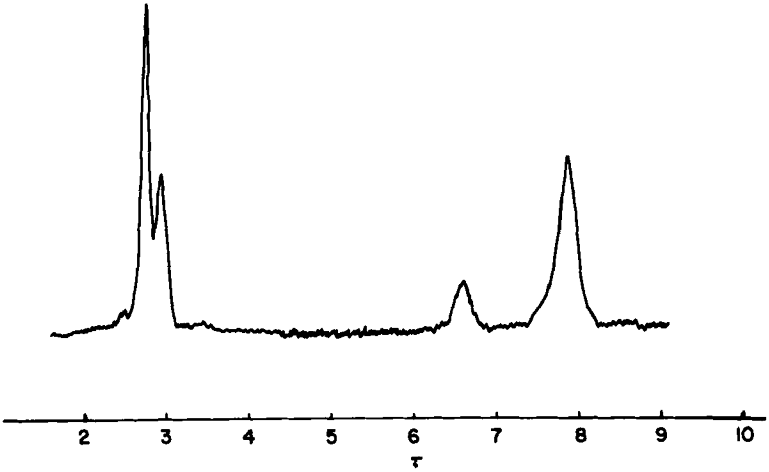

Fig. 1. NMR spectrum of 1:1 alternating styrene–α-chloroacrylonitrile copolymer prepared by complexation with $AlEt_{1.5}Cl_{1.5}$.

The methylene protons belonging to both styrene and α-chloroacrylonitrile units appear together as a single peak centered at 7.88 τ.

Figure 2 presents the NMR spectra of the random styrene–α-chloroacrylonitrile copolymers prepared in bulk uning azobisisobutyronitrile as the initiator at 60°C. The experimental details and the analysis of the copolymers are summarized in Table 1. In Fig. 2, Spectra 2A, 2B, 2C, and 2D represent the S-CA copolymers of different compositions. The Copolymers A, B, and C were run in $CDCl_3$ and D in acetone-d_6 at 70°C.

In general, there are three principal areas of absorption due to the aromatic protons (ca. 2.5-3.5 τ), the α-methine protons of styrene units (ca. 6.5-7.7 τ), and the methylene protons belonging to both S and CA units (ca. 7.7-8.5 τ). It is also evident that as the CA content in the copolymers increases, each of the resonance peaks shifts downfield. This is because each of these resonances is associated with the styrene unit and the downfield shift is due to the deshielding effect of the neighboring CA unit.

The phenyl protons in Spectrum 2A (S/CA = 70/30) appear as two peaks centered at 2.80 and 3.20 τ. These peaks shift downfield in Spectra 2B, 2C, and 2D in which the CA content increases progressively. The peaks in Spectrum 2C (S/CA = 50/50) coincide with the corresponding peak positions in Fig. 1 (alternating copolymer). The phenyl protons appear as a

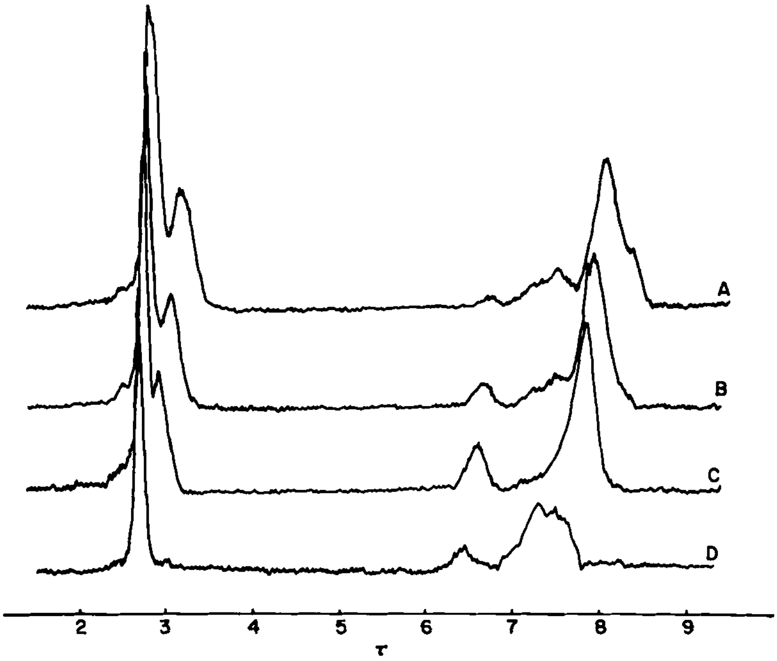

Fig. 2. NMR spectra of random styrene–α-chloroacrylonitrile copolymers prepared with free radical catalyst. Copolymer composition styrene:α-chloroacrylonitrile (mole ratio): (A) 70:30, (B) 61:39, (C) 50:50, (D) 34:66.

single peak in Spectrum 2D (S/CA = 34/66). Since in this copolymer each S unit would be surrounded by CA units, the single peak is possible due to the predominantly pentad configurations CA-CA-S-CA-CA (and CA-CA-S-CA-S).

The methylene protons belonging to both S and CA units appear as a single peak at the highest field strength in the spectrum. In Spectrum 2A this peak is centered at 8.1 τ and progressively shifts downfield with increased CA content in the copolymers (Spectra 2B, 2C, and 2D).

The methine proton resonance appears in the range 6.1-7.7 τ, depending on the composition of the copolymer. In the copolymer having low styrene content (Spectrum 2D) it appears as a single peak at about 6.5 τ whereas other resonance up to 7.7 τ is evident in the spectra of copolymers having higher styrene contents. In these copolymers a part of the methine resonance and the methylene proton resonance appear to be overlapped to some extent.

Table 1. Copolymerization of Styrene and α-Chloroacrylonitrile in Bulk[a]

Copolymer	Styrene (moles)	α-Chloroacrylonitrile (moles)	Conversion (%)	Copolymer composition S:CA mole ratio: Elemental analysis	Copolymer composition S:CA mole ratio: NMR
A	0.48	0.02	4.6	71:29	70:30
B	0.45	0.05	4.2	63:37	61:39
C	0.20	0.20	7.8	50:50	50:50
D	0.05	0.45	4.3	36:64	34:66

[a] AIBN 0.3 mmole, 60°C, 1 hr.

Table 2. Comparison of Observed Methine Resonance Patterns with Calculated Styrene Centered Triad Fractions

Copolymer	$F_{CA\text{-}S\text{-}CA}$ Obsd[a]	$F_{CA\text{-}S\text{-}CA}$ Calcd[d]	$F_{CA\text{-}S\text{-}S}$ Obsd[b]	$F_{CA\text{-}S\text{-}S}$ Calcd[d]	$F_{S\text{-}S\text{-}S}$ Obsd[c]	$F_{S\text{-}S\text{-}S}$ Calcd[d]
A	0.079	0.086	0.434	0.416	0.484	0.498
B	0.267	0.277	0.500	0.499	0.233	0.224
C	0.815	0.812	0.185[e]	0.178	0.000	0.010
D	0.970	0.960	0.030[e]	0.040	0.000	0.000

[a] Fraction of methine resonance observed up to 6.85 τ.

[b] Fraction of methine resonance observed at 6.85-7.50 τ.

[c] 1 - (a + b).

[d] Based on the monomer reactivity ratios [8] $r_S = 0.10$ and $r_{CA} = 0.08$.

[e] Since methylene proton resonance was observed at field strengths less than 7.5 τ, this was taken as 1 - a.

Since the methine proton resonance in the alternating copolymer (Fig. 1) appears as a single peak in the range 6.25-6.85 τ, the resonance in the range up to 6.85 τ is assigned to the methine protons centered in CA-S-CA triads. Since in polystyrene the methine proton resonance overlaps that of the methylene proton resonance and since no resonance is apparent at a field less than 7.5 τ, the resonance beyond 7.5 τ may be assigned to the methine protons centered in S-S-S triads. The resonance in the range 6.85-7.50 τ can then be assigned to the methine protons centered in CA-S-S (and S-S-CA) triads.

The resonance centered at about 6.6 τ was determined directly. The resonance in the range 6.85-7.50 τ was determined directly in copolymers having higher styrene content (A and B). Since in Copolymers C and D, the methine resonance overlapped the methylene proton resonance, this was determined by subtracting the methine resonance centered at 6.6 τ from the total methine resonance expected from the composition of the copolymer. The resonance due to S-S-S triads (beyond 7.5 τ) were determined by subtracting the methine resonance area in the range 6.2-7.5 τ from the total methine resonance expected from the copolymer composition. The observed triad fractions thus obtained were compared with the triad fractions calculated [10] from the reactivity ratios. The results are presented in Table 2 and show good agreement.

Table 3. Probability of Cross-Propagation in S-CA Copolymers

Random copolymer	S/CA mole ratio in feed	$P_{S\text{-}CA}$[a]	$P_{CA\text{-}S}$[b]	P_C[c]
A	24.0	0.294	0.007	0.293
B	9.0	0.526	0.991	0.521
C	1.0	0.901	0.926	0.834
D	0.11	0.980	0.581	0.569

[a] Calculated assuming $r_S = 0.1$ [8].

[b] Calculated assuming $r_{CA} = 0.08$ [8].

[c] $P_C = P_{S\text{-}CA} \times P_{CA\text{-}S}$.

It is also apparent that the NMR spectrum of the free radical initiated equimolar S-CA copolymer (Fig. 2C) is indistinguishable from that of the alternating copolymer (Fig. 1). This is attributed to the fact that Copolymer C has an essentially alternating sequence distribution. This is also apparent from the large value of the probability of cross-propagation as presented in Table 3.

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