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Acrylonitrile Copolymers Using Cobalt Acetylacetonate-Triethylaluminum Initiator System

5. Monomer Sequence Distributions in Acrylonitrile-Styrene Copolymers

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SUMMARY

The reactivity ratios of styrene and acrylonitrile were computed from the ^{13}C-NMR spectra of copolymers prepared using cobalt acetylacetonate -triethylaluminum initiator system and compared with a free radical initiator such as AIBN. The results indicate that polymerization using the former has pronounced free radical characteristics.

INTRODUCTION

In a previous paper (1) we described the synthesis and kinetics of polymerization of styrene-acrylonitrile copolymers using $Co(acac)_3$-$AlEt_3$ initiator system. It was speculated that the catalyst site might possess both coordinate anionic and free radical characteristics. We present in this paper the monomer sequence distributions in these copolymers as studied by ^{13}C-NMR. The bearing of sequence distributions on reaction mechanism is elaborated.

EXPERIMENTAL

The synthesis of styrene-acrylonitrile copolymers was described earlier (1). The relevant details are summarized in Table I. From the yield of the polymer, the monomer composition at the time of quenching the polymerization was deduced and found to be nearly the same as the initial composition. This ensures the applicability of the instantaneous copolymerization model (2) in cases 1, 2 & 3 (Table I).

The synthesis of 1:1 alternating copolymer of styrene and acrylonitrile was performed using $ZnCl_2$. Styrene (0.05 mol) was added to a preformed 1:1 acrylonitrile-zinc chloride complex (0.05 mol) at 50°C. The reaction mixture was quenched with methanol after 4 h. The polymer was purified by dissolving in DMSO and reprecipitation with methanol.

The ^{13}C-NMR spectra were taken on a JEOL FX 100 MHz NMR instrument. The polymers were dissolved in DMSO-d_6 the center peak of which (39.5 ppm) was taken as the internal standard. The pulse angle was 45^{o} and the pulse repetition time was 5 sec which was more than five times the T_1 value for every carbon in the polymer^{2}. The polymer composition was deduced directly from the areas under the signals for the C_1 carbon of the phenyl group and the nitrile carbon of the acrylonitrile unit. The peak intensities were determined by cutting and weighing the various peaks.

Table 1: Synthesis of styrene (S) - acrylonitrile (A) copolymers +)

Sample ref. no.	Initiator Co/Al = 1	Initial monomer feed S/A	Conversion to polymer (%)	Polymer composit S/A	Monomer composit. at quenching time.
1.	$Co(acac)_3$-$AlEt_3$	20/80	10	41/59	18.4/81.6
2.	$Co(acac)_3$-$AlEt_3$	50/50	16	62.6/37.4	47.5/52.5
3.	$Co(acac)_3$-$AlEt_3$	80/20	12	73.2/26.8	80.6/19.4
4.	$ZnCl_2$	50/50	100	50/50	-

+) Intrinsic viscosity ca. 0.2 dl/g

RESULTS AND DISCUSSION

The ^{13}C signals for the C_1 carbon of the phenyl group of the styrene unit and the nitrile carbon of the acrylonitrile unit were triad sensitive (3) and were utilized in all the calculations. The methine carbon of the acrylonitrile unit was also triad sensitive but overlapping between AAA and AAS signals was serious. But the qwuantitative changes in the intensities of the methine carbon signals of the acrylonitrile unit were in agreement with those in nitrile carbon signals.

The triad signal intensities of C_1 and -CN carbons are given in Table 2. The computed intensities based on a first order Markovian model are in good agreement with the experimental ones (Table II). Hence the applicability of a terminal copolymerization model is indicated.

The reactivity ratios of acrylonitrile and styrene were obtained by plotting the average sequence length of the respective monomer versus the monomer feed ratio (4) (Fig. 1 and 2).

The close correspondence of the reactivity ratios in this complex initiator system with those from AIBN initiator system (5) as well as the simple conformity with first order Markovian statistics (the latter finding pointing out the operation of probably a single mechanism) show that the polymerizing end has very pronounced free radical characteristics in the $Co(acac)_3$-$AlEt_3$ initiator system.

Since the original assignment of ^{13}C signals for the styrene-acrylonitrile polymer (3) more detailed assignments have been made by Pichot and Pham (5). The latter authors assigned a signal at 31.8 ppm to the methylene carbon of SA dyad. We synthesized an alternating copolymer of styrene-acrylonitrile using $ZnCl_2$ initiator (Sample referenced no.4, Table 1). While the SAS triad signal was the most intense for this polymer indicating high alternation of the monomers, the signal at 31.8 ppm assigned by Pichot and Pham to the mixed dyad SA was very weak (Fig.3) pointing out the error in assignment. This signal is to be attributed to the methylene carbon of AA dyad and presumably arises from cotacticity effects or tetrad placements as in the case of acrylonitrile-vinyl acetate copolymer (6).

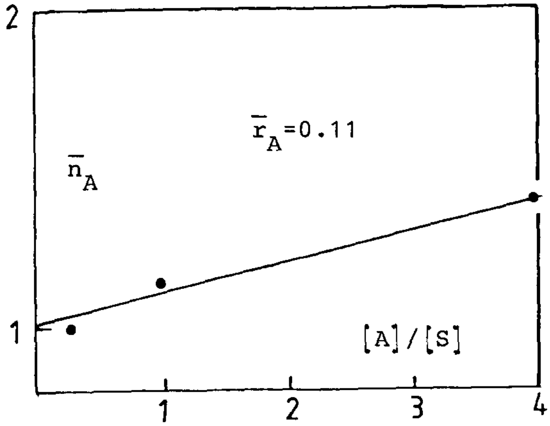

Figure 1: Average sequence length of acrylonitrile ($\bar{n}_A$) versus initial monomer composition ([A]/[S])

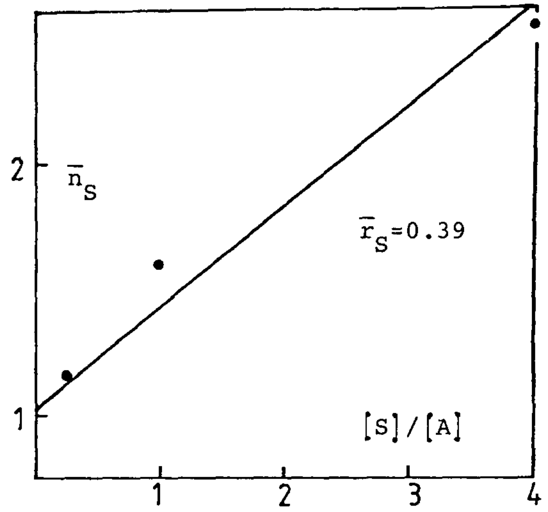

Figure 2: Average sequence length of styrene ($\bar{n}_S$) versus initial monomer composition ([S]/[A])

Figure 3: ^{13}C NMR spectrum of an alternating copolymer 1/1 of styrene and acrylonitrile (sample reference 4 Table 1, see also text)

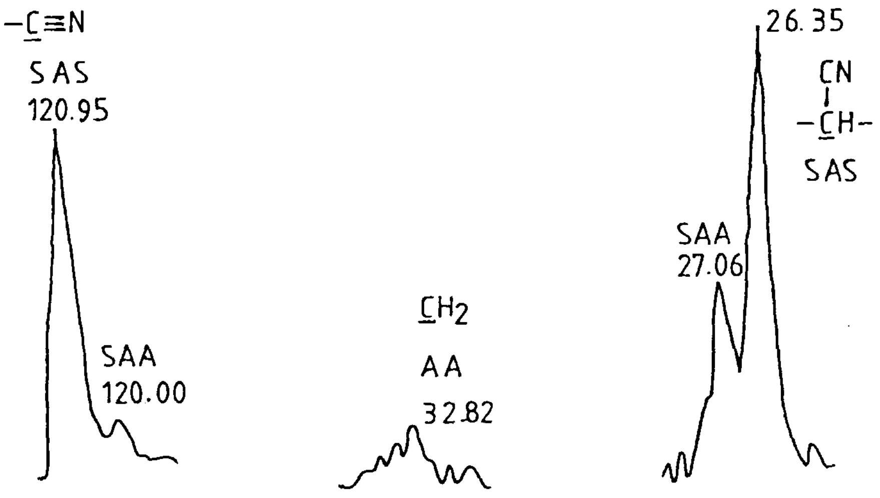

Table 2: Experimental and calculated triad intensities in styrene (S) - acrylonitrile(A) copolymers
Calculated intensities in brackets
P_{AS} = Probability of adding S to A-end of growing polymer

Sample no.	SSS	SSA	ASA	SAS	SAA	AAA	Conditional probabilit.
	.0	.105	.305	.292	.266	.041	.712
1.	(.008)	(.101)	(.341)	(.279)	(.226)	(.046)	P_{AS}= .871
	.079	.302	.243	.299	.054	.021	.872
2.	(.080)	(.271)	(.230)	(.319)	(.094)	(.007)	P_{AS}= .629
	.269	.348	.114	.227	.041	.0	.924
3.	(.259)	(.334)	(.108)	(.255)	(.042)	(.002)	P_{AS}= .933

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REFERENCES

1. V.G. Gandhi, S. Sivaram and I.S. Bhardwaj, J. Macromol. Sci.-Chem; A 18, 1499 (1982).

2. J. Schaefer in "Topics in Carbon-13 Spectroscopy", Vol. 1, ed. by G.C. Levy, Wiley-Interscience, New York 166 (1974).

3. J. Schaefer, Macromolecules, 4,107 (1971).

4. J.L. Koenig, "Chemical Microstructure of Polymer Chains", Wiley-Interscience, New York 101 (1980).

5. C. Pichot and Q. - T. Pham, Makromol. Chem; 180, 2359 (1979).

6. N. Kalyanam, V.G. Gandhi, S. Sivaram and I.S. Bhardwaj, Macromolecules, 15 1636 (1982).

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