Macromolecules **1982**, *15*, 1636–1638

Acrylonitrile Copolymers Using the Cobalt Acetylacetonate–Triethylaluminum Initiator System. 3. Monomer Sequence Distributions†

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Received December 18, 1981

Introduction

Acrylonitrile–vinyl acetate copolymer has been evaluated as a precursor for carbon fibers.[1] FT IR studies of the degradation of an acrylonitrile–vinyl acetate copolymer have demonstrated that the inclusion of approximately 3 mol % vinyl acetate in poly(acrylonitrile) chain increases the rate of degradation.[1]

Previous publications from this laboratory have dealt with kinetic features of the copolymerization of acrylonitrile with vinyl acetate using $Co(acac)_3$–$(C_2H_5)_3Al$ initiator systems.[2] In continuation we now report for the first time a ^{13}C NMR analysis of monomer sequence distribution of copolymer obtained with $Co(acac)_3$–$(C_2H_5)_3Al$ initiator. The results are compared with results for similar copolymers obtained by using AIBN and $ZnCl_2$ as initiators.

Experimental Section

Materials. The synthesis and purification of copolymers using $Co(acac)_3$–$(C_2H_5)_3Al$ and AIBN initiator systems have been previously described.[2] Copolymerization using anhydrous zinc chloride was performed by a procedure described by Chen.[3]

NMR Spectra. ^{13}C NMR spectra were recorded on a JEOL JNM FX-100 spectrometer with an operating frequency of 25 MHz using a 10-mm probe. Copolymers were dissolved in $(CH_3)_2SO$-d_6 (100 °C) or $(CD_3)_2CO$ (50 °C) at a concentration of ca. 10 wt %. The central peak of the $(CH_3)_2SO$-d_6 signals was used as the internal standard (39.5 ppm) and the values reported are corrected to $(CH_3)_4Si$ standard. The pulse width was 7 μs, corresponding to a 45° flip and the pulse repetition time was 5 s. The adequacy of the pulse repetition time is borne out by the excellent agreement between number-average sequence lengths of acrylonitrile ($\bar{n}_A$) calculated from the different spectral regions (methylene carbon dyad signals and acrylonitrile-centered methine carbon triad signals). The quantitative agreement between different n-ads (vide infra) is further proof of adequate repetition times. In fact, no distortions occurred with still shorter repetition times down to 1.2 s. The signal intensities of more mobile carbons (CH_3 etc.) were not utilized for quantitative calculations. Nuclear Overhauser enhancement was assumed to be constant and maximum throughout the polymer chain and is vindicated by agreement in $\bar{n}_A$ values from dyads and triads as well as between n-ads. The intensities of peaks were measured by cutting and weighing peaks.

Results and Discussion

The various copolymers used in this study along with their conditions of preparation are given in Table I. The ^{13}C NMR spectra of copolymer samples (sample nos. 1–3) are given in Figure 1. The complete ^{13}C NMR assignment of copolymer sample no. 1 is given in Table II.

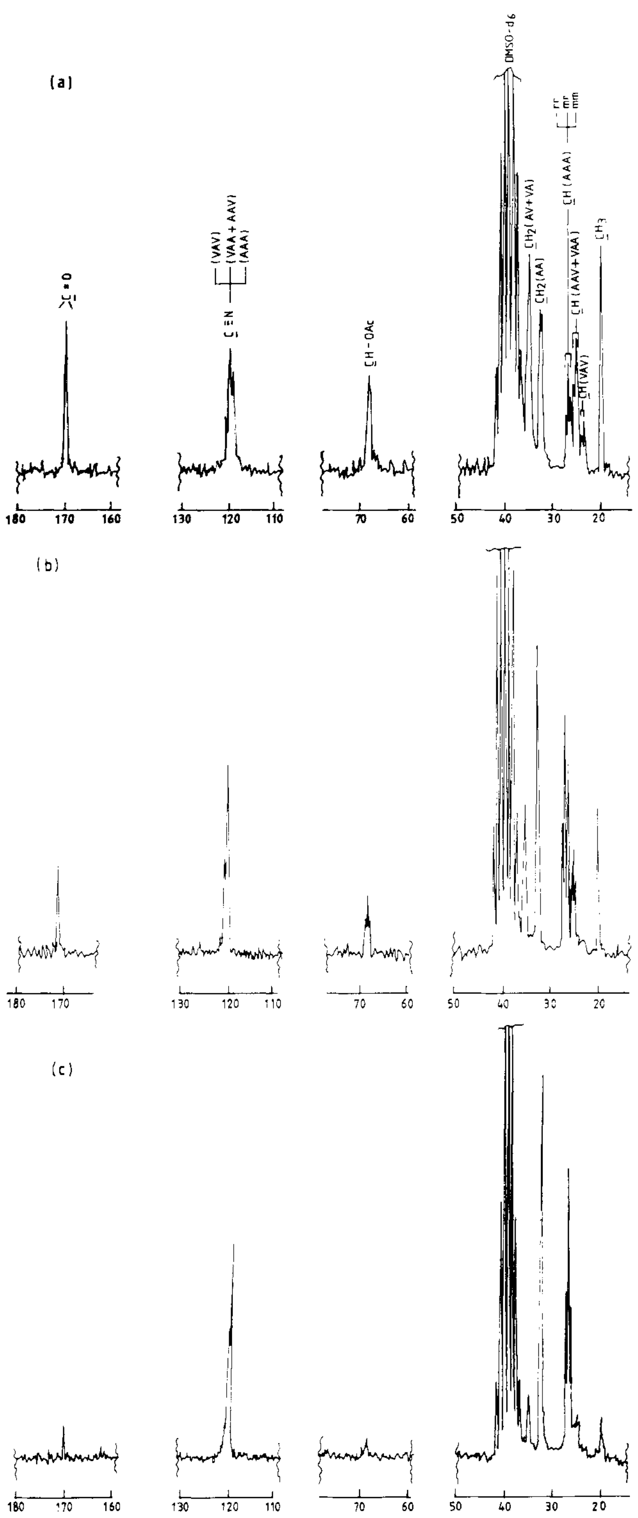

Figure 1. ^{13}C NMR spectra of acrylonitrile–vinyl acetate polymers in $(CH_3)_2SO$-d_6 at 100 °C: (a) sample no. 1; (b) sample no. 2; (c) sample no. 3. (See Table I.)

The signals at 32.70 and 32.94 ppm were assigned to the methylene carbon of the AA dyad in comparison with poly(acrylonitrile). The splitting presumably arises from comonomer placements (tetrads) rather than from tacticity. In the poly(vinyl acetate) homopolymer the methylene carbon of the VV dyad was located at 38.35 ppm, thus interfering with the signals of $(CH_3)_2SO$-d_6. Consequently, NMR spectra were recorded in acetone-d_6, where no such interference occurred. However, in none of the samples examined was there a measurable signal that could be attributed to the VV dyad. The signal at 35.41 ppm was assigned to the AV dyad. The fact that this is located at the midpoint of AA + VV dyads appears to confirm this assignment. The methine carbon of the acrylonitrile unit was remarkably triad sensitive. Splittings in the individual triad signals also occurred, indicating sensitivity to pentad monomer placements and cotacticity effects. The assignment of three peaks, due to tacticity effect, constituting

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† IPCL communication no. 50.

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the AAA triad was directly possible by comparison with poly(acrylonitrile). By increasing the proportion of vinyl acetate in the copolymer, the intensity of the AAA triad decreased and new peaks attributed to the AAV and VAV triads appeared. In copolymer sample no. 7, the peak due to the VAV triad was very intense, as would be expected for an alternating polymer. Also, as expected, the AA dyad signal was very weak and the signal for the AV dyad was very intense. The good separation of the triad resonances for the methine signals of the acrylonitrile unit is presumably due to the incremental γ shielding of the methine carbon by the oxygen of the pendant acetate unit. The assignments were further confirmed by the n-ad relationships

$$(\mathrm{AA}) = (\mathrm{AAA}) + \tfrac{1}{2}(\mathrm{AAV})$$

$$(\mathrm{AV}) = (\mathrm{AAV}) + 2(\mathrm{VAV})$$

In addition, the nitrile carbon of the acrylonitrile unit was triad sensitive, but the peaks were not well separated for quantitative calculations. However, the quantitative changes in the intensity of the triad signals of the nitrile carbons were in conformity with those of methine carbon signals of the acrylonitrile unit. The number-average sequence length of acrylonitrile ($\bar{n}_A$) was calculated from dyad and triad signal intensites (Table III). The number-average sequence length of vinyl acetate ($\bar{n}_V$) is 1 since the VV dyad is not detectable.

$$\bar{n}_A = \frac{(\mathrm{AA}) + \frac{1}{2}(\mathrm{AV})}{\frac{1}{2}(\mathrm{AV})} = \frac{(\mathrm{AAA}) + (\mathrm{AAV}) + (\mathrm{VAV})}{\frac{1}{2}(\mathrm{AAV}) + (\mathrm{VAV})}$$

The carbonyl, methine, and methyl carbons of the vinyl acetate unit appeared as singlets, pointing out the existence of only one type of vinyl acetate centered triad, namely, AVA.

Table I
Synthesis of Acrylonitrile-Vinyl Acetate Copolymers[a]

sample no.	initiator	acrylonitrile in feed, mol %	conversion, %	η_{rel},[c] dL/g
1	$Co(acac)_3$-$(C_2H_5)_3Al$	20	16.3 (1.3)[b]	
2	$Co(acac)_3$-$(C_2H_5)_3Al$	50	15.8 (1.1)	1.287
3	$Co(acac)_3$-$(C_2H_5)_3Al$	80	1.6 (0.1)	1.066
4	AIBN	20	3.8 (0.3)	1.210
5	AIBN	50	11.5 (0.8)	1.099
6	AIBN	80	15.6 (0.9)	1.265
7	$ZnCl_2$	20	11.3 (0.9)	1.453
8	$ZnCl_2$	50	25.2 (1.8)	1.353
9	$ZnCl_2$	80	21.0 (1.3)	1.309

[a] Polymerizations were conducted with 0.05 M initiator concentrations (except in the case of $ZnCl_2$, where a 4 M solution was employed, 1:1 molar acrylonitrile-$ZnCl_2$ complex) in benzene at 40 °C for 4 h. Total reaction volume, 25 mL. [b] Numbers in parentheses are conversions in grams. [c] 0.1% solution in DMF at 30 °C.

Table II
Chemical Shift Assignments for Acrylonitrile-Vinyl Acetate Copolymer Sample No. 1

carbon	sequence assignment[a]	chem shift[b]
C=O	V	169.77
C≡N	VAV	120.71
	AAV	120.00
	AAA	119.30
*C*HOAc	V	68.59
CH_2	AV	35.41
	AA	32.94 32.70
*C*HCN	AAA (rr)	27.29
	AAA (mr)	26.94
	AAA (mm)	26.35
	AAV	25.64 25.17 24.82
	VAV	24.00 23.53
CH_3	V	20.00

[a] A = acrylonitrile, V = vinyl acetate, m = meso, and r = racemic. The notation m or r is omitted when assignments are uncertain due to superimposing influences of comonomer placements on configurational tacticities. [b] Chemical shifts given in ppm relative to the center peak of $(CH_3)_2SO$-d_6, taken to be at 39.5 ppm relative to $(CH_3)_4Si$; probe temperature 100 °C.

The monomer sequence distribution of acrylonitrile–vinyl acetate copolymers obtained using $ZnCl_2$ showed some interesting features. It was observed that the tendency to form an alternating structure was most pronounced only in the presence of excess vinyl acetate (Table III, entry 7). With increasing acrylonitrile in polymer, there was a decrease in the alternating sequences. In the only other study of the same polymer reported earlier, it was concluded based on ^{1}H NMR analysis that the copolymer containing 45–50 mol % vinyl acetate (feed: 25 mol % acrylonitrile, 75 mol % vinyl acetate; 1:1 acrylonitrile–$ZnCl_2$ initiator, 40 °C) had an alternating structure.

It is interesting to note that the microstructures of the polymers prepared by free radical and $Co(acac)_3$–$(C_2H_5)_3Al$ initiatior systems are very similar.

Table III
Monomer Sequence Distribution and Average Sequence Lengths in Acrylonitrile–Vinyl Acetate Copolymers

sample no.	monomer feed, mol %		dyad fractions[a]		triad fractions[a]			$\bar{n}_A$ in copolymer		copolymer compn from NMR,[b] mol %	
	A	V	AV	AA	AAA	AAV	VAV	from dyads	from triads	A	V
1	20	80	0.560	0.439	0.255	0.332	0.128	2.56	2.42	71.34	28.66
2	50	50	0.344	0.656	0.531	0.254	0.043	4.82	4.87	82.90	17.10
3	80	20	0.164	0.836	0.733	0.181		10.10	11.19	91.40	8.86
4	20	80	0.510	0.489	0.309	0.339	0.093	2.92	2.82	74.16	25.84
5	50	50	0.346	0.654	0.522	0.267	0.035	4.78	4.86	82.81	17.19
6	80	20	0.163	0.837	0.760	0.159		11.26	11.59	91.90	8.10
7	20	80	0.838	0.162	0.047	0.246	0.276	1.39	1.42	56.89	43.11
8	50	50	0.680	0.320	0.132	0.372	0.156	1.94	1.93	65.98	34.02
9	80	20	0.403	0.597	0.454	0.230	0.106	3.96	3.58	79.03	20.97

[a] The dyads were normalized to unity; acrylonitrile-centered triads were normalized to the amount of acrylonitrile in the polymer. [b] Obtained from the average sequence lengths from dyads and triads.

Acknowledgment. We acknowledge experimental assistance by A. C. Patel and S. T. Parmar.

References and Notes

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Thermal Reactivity of Poly(styrene peroxide): A Thermodynamic Approach

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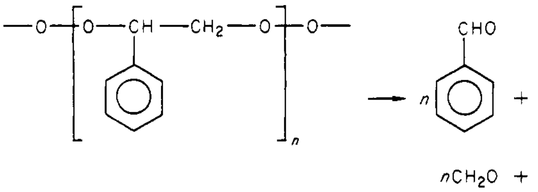
Received April 30, 1982

Polymeric peroxides are an important class of compounds and in the past a significant amount of work has been reported by Mayo et al.[1-3] and Cais.[4] The literature on polymeric peroxides has also been reviewed recently.[5] Poly(styrene peroxide) (PSP) decomposes exothermically; however, no justification for the exothermic nature of the reaction is available. This note attempts to explain the exothermicity of PSP decomposition by thermodynamic considerations.

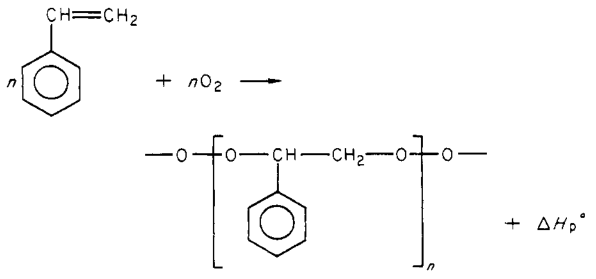
It is known that PSP decomposes to give benzaldehyde and formaldehyde as major products, with the evolution of heat.[2,6] Recent studies from this laboratory using pyrolysis gas chromatography have confirmed that formaldehyde and benzaldehyde are the major products of degradation (95–97%) in the temperature range 120–350 °C.[7] The degradation can be expressed as



(1)

In order to calculate the heat of degradation ($\Delta H_d°$), one must known the heat of formation ($\Delta H_f°$) of PSP. This was evaluated from (i) the heat of polymerization ($\Delta H_p°$) and (ii) the heat of combustion ($\Delta H_c°$).

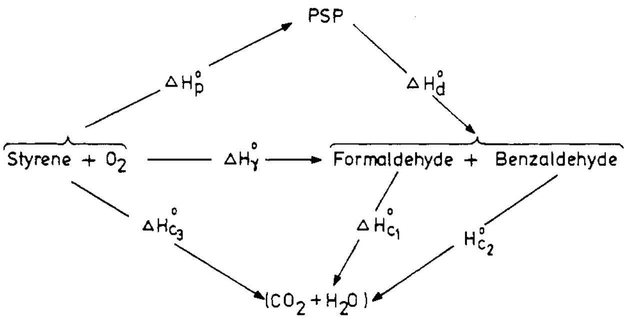
(i) PSP is formed by the reaction of O_2 with styrene:



(2)

In this process a C═C and an O═O bond are broken to form one O–O, one C–C, and two C–O bonds. Using Table II, one calculates the value of $\Delta H_p°$ for PSP to be 20.9 kcal mol^{-1}. However, $\Delta H_p°$ is also dependent upon structural factors. For example, in vinyl polymerization the breakage of one C═C bond gives rise to two C–C bonds and the heat evolved in the process is 19.8 kcal mol^{-1}, as compared to 16.8 kcal mol^{-1} for the experimental value of $\Delta H_p°$ for polystyrene (Table I). Taking into consideration the structural factors, we therefore take the actual $\Delta H_p°$ value for PSP to be 18 kcal mol^{-1}. Using this value and the $\Delta H_f°$ for styrene, we calculate the $\Delta H_f°$ for PSP to be 7 kcal mol^{-1} and that for PS to be 8 kcal mol^{-1}.

Scheme I



(ii) $\Delta H_c°$ of PSP was experimentally measured with a Parr 1243 automatic adiabatic bomb calorimeter attached to a 1680 master control. Correction for the formation of HNO_3 and the heat of combustion of the fuse wire and cotton was made. The instrument was calibrated with standard benzoic acid pellets supplied by Parr. The experimental value of $\Delta H_c°$ for PSP was found to be 1032 ± 5 kcal mol^{-1}. Utilizing these data and the $\Delta H_f°$'s for CO_2 and H_2O, we calculate the $\Delta H_f°$ for PSP to be 6 kcal mol^{-1}.

A mean value of 6.5 kcal mol^{-1} was presumed to be the heat of formation of PSP on the basis of the $\Delta H_f°$ for PSP obtained from the data of heat of polymerization and the heat of combustion (7 and 6 kcal mol^{-1}, respectively). The $\Delta H_f°$ evaluated independently from the heat of polymerization and $\Delta H_c°$ are similar, showing consistency in the derived $\Delta H_f°$ value.

$\Delta H_d°$ for PSP was calculated by four different procedures.

(1) Using $\Delta H_f°$, we calculated theoretically from eq 1 the heat change during PSP decomposition.

$$\Delta H_f°(\mathrm{PSP}) \rightarrow \Delta H_f°(C_6H_5CHO) + \Delta H_f°(CH_2O) + \Delta H_d° \qquad (3)$$

It was found to be −52 kcal mol^{-1}.

(2) $\Delta H_d°$ was calculated from bond dissociation energies. During the process of PSP degradation (eq 1) one C–C bond and one C–O bond are broken while two C–O bonds are converted to two C═O bonds, and formaldehyde is vaporized. The calculated enthalpy change ($\Delta H_d°$) for this process is −50.3 kcal mol^{-1}.

(3) Scheme I together with Hess' law was used. $\Delta H_{c_3}°$, the heat of combustion of styrene (−1050 kcal mol^{-1}), was obtained from the following equation, employing $\Delta H_f°$ from Table I:

$$C_8H_8(\mathrm{l}) + 10O_2 \rightarrow 8CO_2 + 4H_2O + \Delta H_{c_3}° \qquad (4)$$

Since

$$\Delta H_c°(\mathrm{styrene}) \rightarrow \Delta H_c°(\mathrm{PS}) - \Delta H_p°(\mathrm{styrene} \rightarrow \mathrm{PS}) \qquad (5)$$

and $\Delta H_c°$ and $\Delta H_p°$ for PS are known (Table I), $\Delta H_c°$ of styrene was again obtained as 1052 kcal mol^{-1}. The reported value of $\Delta H_c°$ for styrene (1019 kcal mol^{-1}) in ref 8 thus seems to be incorrect. $\Delta H_r°$ as represented in Scheme I was obtained from $\Delta H_f°$ data (Table I) as 70.3 kcal mol^{-1}. Using Tables I and II, we also calculated independently $\Delta H_r°$ = 71.6 kcal mol^{-1}. $\Delta H_f°$ was thus taken

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