Full Assignment of Cyano- and Methine-Carbon Peaks in 50 MHz ^{13}C NMR Spectrum and Determination of Sequence Distribution of Acrylonitrile/ Vinylidene Chloride Copolymer

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ABSTRACT: An attempt was made for a radically polymerized acrylonitrile/vinylidene chloride (AN/VDC) copolymer 1) to establish a full assignment of CN and CH peaks over an entire range of ^{13}C NMR spectra and 2) to evaluate, based on the assignment, the triad and pentad sequences for an AN/VDC copolymer. For this purpose, the stereoregularity of an AN sequence and an interaction between neighboring AN and VDC monomers, which induces the double bond nature of CN group of AN, were considered. The predicted relative chemical shifts for all possible pentad sequences were expressed in terms of parameters representing the electro-magnetical influence on the centered CN or CH carbon and the peak assignment was carried out by comparing the experimental peak position and the order of the relative chemical shifts with those predicted. The peak fractions calculated by assuming that the pentad sequence distribution first obeyed 1st order Markov statistics and then the distribution of continuous AN monomer sequence part obeyed Bernoullian statistics were found to be in good agreement with the experimental peak fractions. Analysis on reactivity ratio supported the existence of the above interactions between neighboring AN and VDC monomers.

KEY WORDS Acrylonitrile / Vinylidene Chloride / Sequence Distribution /
 ^{13}C NMR / Copolymer / 1st Order Markov Statistics / Reactivity Ratio /

Acrylonitrile (AN)/vinylidene chloride (VDC) copolymer (AN/VDC copolymer) is an industrially interesting polymer, because of its excellent fiber-formability together with high non-flammability. Recently, Kamide *et al.*¹ studied by viscometry and light scattering some dilute solution properties of an AN/VDC copolymer with 58 weight percent in AN, clarifying the molecular characteristics of this polymer. In order to confirm the constancy of the chemical compositions of all fractions employed, they only estimated the relative mole fractions of V-centered triads of VVV, VVN, and NVN and N-centered triads of NNN,

NNV, and VNV from the intensities of the peaks for the dichloro-substituted carbons (CCl_2) of VDC and methine (CH) carbons of AN, respectively. Here, V and N mean VDC and AN. More detailed evaluation of the higher order (tetrad, pentad, ...) sequence distribution is a significantly effective help to understand well the copolymerization mechanism and probably to establish the relations between the sequence distribution and the polymer properties. Ito and associates² are probably the first to evaluate the sequence distribution of AN/VDC copolymer by NMR method. They estimated the relative

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amounts of diads (NN, NV, and VV) from the methylene (CH_2) proton peaks. Bailey and Henrichs³ measured diad, triad and pentad sequence distributions of AN/VDC copolymers (ten samples with substantially different AN ratio) by ^{13}C NMR, who for this purpose made the peak assignment of the CCl_2 carbons in VDC monomer units, showing the existence of the triad-sensitive peaks for NVN, NVV, and pentad-sensitive peaks for NVVVN, NVVVV, and VVVVV. They estimated the relative amounts of various V-centered triads and also made an assignment of CH_2 carbon peaks, from which the relative amounts of three diads (NN, NV, and VV) were determined. Unfortunately, they refrained from rigorous peak assignment on nitrile (CN) and methine (CH) carbons belonging to AN monomer unit, due to the complexity of the NMR patterns, probably induced by possible stereoregular heterogeneity of AN sequence. Later, König and Wendisch⁴ made an assignment on the CN and CH carbon NMR peaks originating from the continuous AN sequence part in AN/VDC copolymer with molar fraction of AN 73.6%, prepared by continuous suspension polymerization and estimated the triads distributions, concluding a slight preference of isotactic triad against the syndiotactic triad, as found for polyacrylonitrile (PAN) prepared by free radical polymerization.

Recently, we⁵ carried out successfully, by considering the electro-magnetical influence on CN carbons induced by the interaction of adjacent CN groups arranged in *meso* (*m*) configuration, a full assignment on CN carbon peaks of PAN, based on pentad tacticity. On the basis of this assignment we showed that the stereoregularity of PAN prepared by polymerization with a redox catalyst (R-PAN) obeyed Bernoullian statistics. Thereafter, Kamide *et al.*⁶ interpreted an unexpectedly large chain conformation parameter of highly isotactic PAN with the content of *mmmm* sequence of 0.37 in terms of the rigidity of the chain due to

intra-interactions between neighboring CN groups in *m* sequence.

Although numerous studies on the sequence distribution in AN/VDC copolymer have been published hitherto, a full and reasonable assignment of CN and CH carbon peaks in ^{13}C NMR spectrum has not yet been established. This point motivated our present work as an extension of the previous work.⁵ We made full assignment on CN and CH carbon peaks in an AN/VDC copolymer by considering the stereoregularity of AN sequence together with a possible interaction between neighboring AN and VDC residues and to estimate the relative amount of possible pentad sequences in an AN/VDC copolymer.

EXPERIMENTAL

A mixture of AN and VDC (AN/VDC = 72/28, mol/mol, total monomer weight 180 grams) was polymerized in a 540 ml of dimethylformamide (DMF) by free radical solution polymerization at 50°C for 2 h, using azobisisobutyronitrile as an initiator. The AN/VDC copolymer polymerized thus obtained was isolated by pouring the above DMF solution into approximately 5 liters of methanol. The mixture was stirred for 10 min and the precipitate was filtered through, rinsed with methanol, filtered again, and then dried at room temperature and *in vacuo* 30 h at 50°C. The polymerization yield was 71 wt%. One of the fractions (Code AV-1-6), fractionated by successive solution fractionation method using dimethyl sulfoxide (DMSO) and toluene as solvent and nonsolvent, respectively, was used. The weight-average molecular weight $\bar{M}_w$ of the sample was determined as 9.0×10^4 from light scattering data.¹

^{13}C NMR Measurement

^{13}C NMR measurement on the AN/VDC copolymer was made on a FT-NMR spectrometer (JEOL FX-200) using a 1/2 (by volume at 25°C) mixture of DMSO/ $\text{DMSO}-d_6$ as sol-

Figure 1. ^{13}C NMR spectrum of an entire region for an acrylonitrile/vinylidene chloride copolymer.

vent under the operating conditions as follows: NNE mode, pulse delay time 6.5 s, 45° pulse, sampling time 1 s, irradiation time $6.5\ \mu\text{s}$, accumulation 64×120 , data point 16 K, temperature 80°C , internal reference TMS.

RESULTS AND DISCUSSION

Figure 1 shows the entire ^{13}C NMR spectrum of the AN/VDC copolymer in $\text{DMSO}/\text{DMSO}-d_6$. Many CN carbon peaks are seen in the range 119–122 ppm and the corresponding CH carbon peaks also appear in a very complex manner in the range 24–28 ppm. According to the peak assignment on the dichloro-substituted carbon (CCl_2), made by Bailey and Henrichs,³ the peak at 91 ppm was assigned to the centered VDC carbon in NVN sequence, peaks around 88 ppm, to that in VVN and the peaks around 83 ppm, to that in VVV. Seven CH_2 carbon peak envelopes, appearing in the range 60–33 ppm were assigned from lower magnetic field to the centered CH_2 carbons in VVVN, VVNV, VVNN+NVNV, NVNN, VNNV, VNNN, and NNNN, according to the assignment carried out by König and Wendisch.⁴ Chemical shifts and peak intensities of all the peaks separable on the ^{13}C NMR spectrum in CH_2 and CCl_2 carbon peak regions are listed in Table I. Here, peak intensities are normalized as 100% within each

Table I. Observed chemical shifts and their peak intensities in the CCl_2 and CH_2 carbon regions^a

Carbon species	Triad or tetrad sequence	Chemical shifts/ppm	Peak intensity (weight fraction)
$-\text{CCl}_2-$	VVV	82.2 ₆ 83.8 ₀	0.05 ₃
	VVN	88.1 ₃ 88.3 ₂	0.24 ₄
	NVN	91.0 ₆	0.70 ₃
	NNNN	33.0 ₆	0.24 ₅
$-\text{CH}_2-$	VNNN	33.8 ₃ 34.0 ₂ 34.1 ₀	0.20 ₃
	VNNV	35.0 ₀ 35.1 ₄ 35.2 ₈	0.04 ₇
	NVNN	47.9 ₇ 48.2 ₂ 48.2 ₈	0.25 ₀
	VVNN, NVNV	40.0 ₈ 49.2 ₄ 49.3 ₃	0.16 ₇
	VVNV	50.0 ₃ 50.3 ₇	0.02 ₉
	NVVN	60.2 ₀	0.03 ₄
	NVVV	60.8 ₀	0.02 ₂
	VVVV	—	—

^a NNNN contains other 6 shoulder peaks; VNNN, 3 other peaks; VNNV, 3 to 4 other peaks; VVNN and NVNV, 2 other peaks.

Figure 2. a: Magnified ^{13}C NMR spectrum of CN carbon region. b: Magnified ^{13}C NMR spectrum of CH carbon region.

carbon belonging to the same species (*i.e.*, CH_2 and CCl_2 carbons).

Figure 2 shows the magnified ^{13}C NMR spectra for CN (a) and CH (b) carbon regions. The CN carbon region seems to roughly consist of 5 envelopes with at least 9 peaks. The CH carbon region also seems to consist of 6 envelopes with at least 10 peaks. Chemical shifts and their intensities are listed in the 4th and 5th columns of Tables II and III, respectively. Three CN carbon peaks at 119.5, 119.8, and 120.1 ppm and three CH carbon peaks at 27.9, 27.4, and 26.9 ppm were already observed for PAN/DMSO- d_6 system in our previous work⁵ and are responsible for syndiotactic triad (*S*), heterotactic triad (*H*) and isotactic triad (*I*) peaks, respectively.

The peak assignment on CCl_2 carbon carried out by Bailey and Henrichs³ indicated that a N monomer unit adjacent to the centered V gives considerable lower magnetic field shift (about 3.4–3.8 ppm) for the CCl_2 carbon. This means that primarily electron density on the CCl_2 carbon becomes low, probably due to donation of lone pair electron on chlorine, (Cl) atom to N monomer (especially, CN and CH carbon groups), leading to definite interaction

Figure 3. Schematic representation of a typical interaction between Cl in V monomer and adjacent N monomer. ○, carbon; ●, hydrogen; ◐, chlorine; ◑, nitrogen.

between Cl in V monomer and adjacent N monomer. An example of a typical interaction working in AN/VDC copolymer is illustrated in Figure 3. The interaction between a given Cl atom and adjacent AN might take place irrespective of the configuration of the adjacent AN monomer because VDC has two Cl atoms in its monomer unit. The lowering in electron density on CCl_2 carbon is obviously greater for the centered CCl_2 carbon in NVN than that in NVV. Contrary to this, in consideration of the N monomer in the center of the sequences, the above interaction may give several electromagnetic influences on CN and CH carbons of AN monomer unit in the center of any triads

Table II. Pentad sequence distribution in the CN carbon region of an AN/VDC copolymer^a

Sequence	Relative chemical shifts	Order	Chemical shifts/ppm	Weight fraction	
				Obsd	Calcd
V V N V V :	$\delta + 2\sigma_{V_1}$	1	121.3 ₀	0.01 ₁	0.00 ₄
N V N V V :	$\delta + 2\sigma_{V_1} - \sigma_{nv}$	2	121.1 ₆	0.03 ₇	0.03 ₁
N V N V N :	$\delta + 2\sigma_{V_1} - 2\sigma_{nv}$	3	121.0 ₃	0.07 ₆	0.06 ₁
				$\Sigma 0.12_4$	$\Sigma 0.09_6$
V V N ^m N ^m N :	$\delta + \sigma_2 + \sigma_{V_1}$	1	120.7 ₀		0.01 ₆
V V N ^m N V :	$\delta + \sigma_{mv} + \sigma_{V_1}$	1		0.03 ₁	0.01 ₄
N V N ^m N V :	$\delta + \sigma_{mv} + \sigma_{V_1} - \sigma_{nv}$	2	120.6 ₀		0.05 ₅
N V N ^m N ^m N :	$\delta + \sigma_2 + \sigma_{V_1} - \sigma_{nv}$	2		0.08 ₇	0.06 ₄
V V N ^m N ^r N :	$\delta + \sigma_1 + \sigma_{V_1}$	2	120.4 ₉		0.01 ₅
N V N ^m N ^r N :	$\delta + \sigma_1 + \sigma_{V_1} - \sigma_{nv}$	3		0.08 ₈	0.05 ₉
				$\Sigma 0.20_6$	$\Sigma 0.22_3$
N ^m N ^m N ^m N ^m N :	$\delta + 2\sigma_2$	1 (1)	120.2 ₈		0.01 ₆
V N ^m N ^m N ^m N :	$\delta + \sigma_2 + \sigma_{mv}$	1 (1)		0.03 ₇	0.02 ₈
V N ^m N ^m N V :	$\delta + 2\sigma_{mv}$	1 (1)	120.1 ₅		0.01 ₂
N ^r N ^m N ^m N ^m N :	$\delta + \sigma_1 + \sigma_2$	2 (2)		120.1 ₅	
V N ^m N ^m N ^r N :	$\delta + \sigma_1 + \sigma_{mv}$	2 (2)	120.1 ₅		
V V N ^r N ^m N :	$\delta + \sigma_{V_1} + \varepsilon$	2 (2)		120.1 ₅	0.10 ₅
V V N ^r N V :	$\delta + \sigma_{V_1} + \varepsilon_V$	2 (2)	0.01 ₃		
N ^r N ^m N ^m N ^r N :	$\delta + 2\sigma_1$	3 (2)	120.0 ₅		0.01 ₄
V V N ^r N ^r N :	$\delta + \sigma_{V_1}$	3 (2)		120.0 ₅	
N V N ^r N ^r N :	$\delta + \sigma_{V_1} - \sigma_{nv}$	4 (3)	120.0 ₅		
N V N ^r N ^m N :	$\delta + \sigma_{V_1} + \varepsilon - \sigma_{nv}$	4 (3)		120.0 ₅	0.18 ₈
N V N ^r N V :	$\delta + \sigma_{V_1} + \varepsilon_V - \sigma_{nv}$	4 (3)			
				$\Sigma 0.33_0$	$\Sigma 0.33_2$
N ^m N ^r N ^m N ^m N :	$\delta + \sigma_2 + \varepsilon$	1 (1)	119.8 ₀		0.03 ₀
V N ^r N ^m N ^m N :	$\delta + \sigma_2 + \varepsilon_V$	1 (1)		119.8 ₀	
N ^m N ^r N ^m N V :	$\delta + \sigma_{mv} + \varepsilon$	1 (1)	119.8 ₀		0.09 ₁
V N ^r N ^m N V :	$\delta + \sigma_{mv} + \varepsilon_V$	1 (1)		119.7 ₂	
N ^m N ^r N ^m N ^r N :	$\delta + \sigma_1 + \varepsilon$	2 (2)	119.7 ₂		
N ^r N ^r N ^m N ^m N :	$\delta + \sigma_2$	2 (2)		119.7 ₂	0.14 ₄
N ^r N ^r N ^m N V :	$\delta + \sigma_{mv}$	2 (2)	119.7 ₂		
V N ^r N ^m N ^r N :	$\delta + \sigma_1 + \varepsilon_V$	2 (2)		119.7 ₂	
N ^r N ^r N ^m N ^r N :	$\delta + \sigma_1$	3 (2)			
				$\Sigma 0.23_5$	$\Sigma 0.23_5$
N ^m N ^r N ^r N ^m N :	2ε	1	119.5 ₅		0.01 ₄
V N ^r N ^r N ^m N :	$\varepsilon_V + \varepsilon$	1		119.5 ₅	0.01 ₄
V N ^r N ^r N V :	$2\varepsilon_V$	1	119.4 ₈		
V N ^r N ^r N ^r N :	ε_V	2		119.4 ₈	
N ^r N ^r N ^r N ^m N :	ε	2	119.4 ₈		0.04 ₉
N ^r N ^r N ^r N ^r N :	0	3		119.4 ₁	
				$\Sigma 0.10_5$	$\Sigma 0.10_8$

Table III. Pentad sequence distribution in the CH carbon region of an AN/VDC copolymer

Sequence	Relative chemical shifts	Order	Chemical shifts/ppm	Weight fraction		
				Obsd	Calcd	
N' N' N' N' N :	0	1	} 27.8 ₈	0.06 ₅	0.01 ₂	} 0.05 ₂
N' N' N' N' N'' N :	0	1			0.02 ₆	
N'' N' N' N' N'' N :	0	1			0.01 ₄	
V N' N' N' N' N :	-γ _{V₂}	2	} 27.7 ₇	0.04 ₃	0.02 ₂	} 0.04 ₆
V N' N' N' N'' N :	-γ _{V₂}	2			0.02 ₄	
V N' N' N' N V :	-2γ _{V₂}	3	27.7 ₀	0.00 ₉	0.01 ₁	0.01 ₁
				Σ 0.11 ₇	Σ 0.10 ₉	
N' N' N'' N' N' N :	δ' - ω - γ	1 (1)	} 27.4 ₂	0.18 ₁	0.02 ₆	} 0.16 ₂
N'' N' N' N'' N' N' N :	δ' - ω - γ	1 (1)			0.02 ₈	
N' N' N' N'' N'' N' N :	δ' - ω - γ	1 (1)			0.02 ₈	
N'' N' N' N'' N'' N'' N :	δ' - ω - γ	1 (1)			0.03 ₀	
V N' N'' N' N' N' N :	δ' - ω - γ - γ _{V₂}	2 (1)			0.02 ₄	
V N' N'' N'' N' N' N :	δ' - ω - γ - γ _{V₂}	2 (1)	} 27.2 ₅	} 0.06 ₅	0.02 ₆	} 0.07 ₃
N' N' N' N'' N V :	δ' - ω - γ - ω _{mv} - γ _{mv}	2 (2)			0.02 ₄	
N'' N' N' N'' N V :	δ' - ω - γ - ω _{mv} - γ _{mv}	2 (2)			0.02 ₆	
V N' N' N'' N V :	δ' - ω - γ - ω _{mv} - γ _{mv} - γ _{V₂}	3 (2)	27.2 ₀		0.02 ₃	
				Σ 0.24 ₅	Σ 0.23 ₅	
N' N'' N'' N' N' N :	δ' - 2ω - 2γ	1	} 26.9 ₀	0.07 ₂	0.01 ₄	} 0.06 ₀
N' N'' N'' N'' N' N' N :	δ' - 2ω - 2γ	1			0.03 ₀	
N'' N'' N'' N'' N'' N' N' N :	δ' - 2ω - 2γ	1			0.01 ₆	
V N'' N'' N' N' N' N :	δ' - 2ω - 2γ - ω _{mv} - γ _{mv}	2	} 26.8 ₀	0.05 ₃	0.02 ₆	} 0.05 ₄
V N'' N'' N'' N' N' N :	δ' - 2ω - 2γ - ω _{mv} - γ _{mv}	2			0.02 ₈	
V N'' N'' N' N V :	δ' - 2ω - 2γ - 2ω _{mv} - 2γ _{mv}	3	26.7 ₅	0.01 ₀	0.01 ₂	0.01 ₂
				Σ 0.13 ₅	Σ 0.12 ₆	
N V N' N' N' N :	δ' - ω _V + ω _{NV} - γ _V - γ' _V	1	} 26.3 ₀	0.19 ₄	0.05 ₄	} 0.19 ₆
N V N' N'' N' N' N :	δ' - ω _V + ω _{NV} - γ _V - γ' _V	1			0.05 ₉	
V V N' N' N' N' N :	δ' - ω _V - γ _V	1			0.01 ₃	
V V N' N' N'' N' N' N :	δ' - ω _V - γ _V	1			0.01 ₅	
N V N' N' N V :	δ' - ω _V + ω _{NV} - γ _V - 2γ' _V	1			0.05 ₁	
V V N' N' N V :	δ' - ω _V - γ _V - γ _{V₂}	2	26.1 ₅	0.00 ₈	0.01 ₃	0.01 ₃
				Σ 0.20 ₂	Σ 0.20 ₉	
N V N'' N' N' N :	δ' - ω - γ - ω _V + ω _{NV} - γ _V - γ' _V	1	} 25.8 ₀	0.09 ₆	0.05 ₉	} 0.15 ₄
N V N'' N'' N' N' N :	δ' - ω - γ - ω _V + ω _{NV} - γ _V - γ' _V	1			0.06 ₄	
V V N'' N' N' N' N' N :	δ' - ω - γ - ω _V - γ _V	1			0.01 ₅	
V V N'' N'' N' N' N' N :	δ' - ω - γ - ω _V - γ _V	1			0.01 ₆	
N V N'' N' N V :	δ' - ω - γ - ω _V + ω _{NV} - γ _V - γ' _V - γ _{mv}	2	} 25.7 ₀	0.10 ₁	0.05 ₅	} 0.06 ₉
V V N'' N' N V :	δ' - ω - γ - ω _V - γ _V - γ _{mv}	2			0.01 ₄	
				Σ 0.19 ₇	Σ 0.22 ₃	
N V N V N V N :	δ' - 2ω _V + 2ω _{NV} - 2γ _V - 2γ' _V	1	} 24.8 ₀	0.10 ₃	0.06 ₁	} 0.09 ₆
N V N V N V V :	δ' - 2ω _V + ω _{NV} - 2γ _V - γ' _V	1			0.03 ₁	
V V N V N V V :	δ' - 2ω _V - 2γ _V	1			0.00 ₄	
				Σ 0.10 ₃	Σ 0.09 ₆	

or pentads. The following parameters expressing the electromagnetical influence on central AN monomer are considered in the same procedure used for PAN.⁵

For CN carbon:

- ε : deshielding effect⁵ by an induced magnetic field from double bond nature of m sequence in $\text{N}^m\text{N}^*\text{N}^*$ (* means central) (0.07—0.12 ppm)⁵
- ε_v : deshielding effect by an induced magnetic field from double bond nature in VN sequence connected to the central N unit in r arrangement (VN^*N^*) ($\approx \varepsilon$)
- σ_1 : electron density decreasing effect induced by double bond nature of CN from $\text{N}^r\text{N}^m\text{N}^*$ sequence (0.31—0.41 ppm)⁵
- σ_2 : electron density decreasing effect induced by stronger double bond nature of CN from $\text{N}^m\text{N}^m\text{N}^*$ sequence (0.28—0.52 ppm)⁵
- σ_{v1} : electron density decreasing effect from VN^* sequence induced by double bond nature of CN (0.65—0.75 ppm $\approx 2\sigma_1$)
- σ_{mv} : apparent electron density decreasing effect from VN^mN^* sequence
- $-\sigma_{nv}$: apparent electron density increasing effect on NVN^* sequence. Here, V monomer gives its lone pair electron to both sides of N monomers and then, the double bond nature of N^* diminishes, compared with that of N^* in VVN^* (Cl atom in VV had no interaction with each other)
- δ : an elimination of the shielding effect existed in isolated CN (*i.e.*, CN in $\text{N}^r\text{N}^*\text{N}^*$) by introduction of double bond nature.⁵ This kind of elimination effect can be occurred on CN carbon in the centered N unit in various sequences $\{\text{N}^m\text{N}^m\text{N}$, VN^mN , VNV , VN^rN , $\text{N}^r\text{N}^m\text{N}$, here

suffix m and r between two N monomer units denote the configuration m (*meso*) or r (*racemo*) (≈ 0 ppm)

For CH carbon:

- $-\gamma$: shielding effect from circular current of double bond nature of CN in N^mN^* sequence on CH in *-marked N unit.
- $-\gamma_v$: the same effect described above in VN^* sequence.
- $-\gamma_{v2}$: the same effect described above in VN^rN^* sequence and this effect might be cancelled in $\text{VN}^r\text{N}^m\text{N}$.
- $-\gamma'_v$: additional shielding effect on $-\gamma_v$ in NVN^* .
- $-\gamma_{mv}$: additional shielding effect on $-\gamma$ in VN^mN^* .
- $-\omega$: apparent electron density increasing effect on CH carbon in N^mN^* sequence by lowering of the electronegativity of CN caused by transfer of triple bond to double bond nature
- $-\omega_v$: the same effect described above in VN^* .
- $-\omega_{mv}$: additional electron density increasing effect on $-\omega$ in VN^mN^* sequence.
- ω_{nv} : apparent electron density decreasing effect appearing in VN^* by addition of a N unit to V.
- δ' : an elimination of the shielding effect existed in isolated CN (triple bond) group (≈ 0).

Concerning the parameters on CH carbon, we considered the experimental fact⁵ that three peaks for CH carbon centered at the triad sequences of PAN do not split even if two AN monomer units are added to the both sides of a given triad sequence in either the r or m arrangement.

The relative chemical shifts of CN and CH carbons in the center of the triads expressed by above parameters are collected in the 2nd and 4th columns of Table IV, respectively. Such an

Table IV. Relative chemical shifts for base triads and their orders from a lower magnetic field

Triad sequence	CN carbon		CH carbon	
	Chemical shifts	Order	Chemical shifts	Order
N' N' N	0	5	0	1
N' N" N	$\delta + \sigma_1$	4	$\delta' - \omega - \gamma$	2
N" N" N	$\delta + 2\sigma_1$	3	$\delta' - 2\omega - 2\gamma$	3
V N' N	$\delta + \sigma_{v_1}$	3	$\delta' - \omega_v - \gamma_v$	4
V N" N	$\delta + \sigma_1 + \sigma_{v_1}$	2	$\delta' - \omega - \gamma - \omega_v - \gamma_v$	5
V N V	$\delta + 2\sigma_{v_1}$	1	$\delta' - 2\omega_v - 2\gamma_v$	6

empirical parameter expression of the chemical shifts has been proposed by some authors for several compounds.⁷⁻⁹ For CN carbon, the central CN carbon in a *mmmm* sequence of PAN appeared at the lowest magnetic field (120.11 ppm⁵), but Table II shows the lowest magnetic field peak at 121.0–121.3 ppm, being far lower than the peak for *mmmm* sequence of PAN. This means that the peak at 121.0–121.3 (central peak 121.2 ppm) ppm can be assigned to the central CN carbon peak of VN" N or VNV sequence. Since the CN carbon peak for the *rr* sequence (standard peak for calculation of the relative chemical shifts) of PAN was found at 119.4 ppm,⁵ the difference (1.8 ppm) in chemical shifts between the lowest magnetic field peak and the peak for CN carbon for *rr* sequence of PAN should correspond to the relative chemical shifts either $\delta + \sigma_{v_1} + \sigma_1$ for VN" N or $\delta + 2\sigma_{v_1}$ for VNV. We have already evaluated $\sigma_1 = 0.31$ – 0.41 and $\delta = 0.03$ – 0.06 ppm for R-PAN.⁵ Thus, the lowest magnetic field peak envelope observed for CN carbon in Figure 2a can be regarded as the peak for VNV triad and σ_{v_1} is estimated to be 0.65 – 0.75 ppm. Then, an relation $\sigma_{v_1} \approx 2\sigma_1$ is expected to hold experimentally for AN/VDC copolymer. If this relation is valid the relative chemical shifts expressed by parameters for N" N" N and VN' N should be the same; in other words, a heavy overlapping of these two envelopes is expected. Now, all the parameters employed in expressing the relative chemical shifts of CN carbons

of triad sequences are reasonably estimated: $\delta \approx 0$, $\sigma = 0.31$ – 0.41 and $\sigma_{v_1} = 0.65$ – 0.75 . Then, the order of these chemical shifts in CN carbon region can be definitely determined. The results are: VNV > VN" N > VN' N ~ N" N" N > N" N' N > N' N' N from lower magnetic field as shown in 3rd column of Table IV.

The highest magnetic field peak in CH carbon region for AN/VDC copolymer is observed at 24.8 ppm (Figure 2b and Table III), which is significantly different from that (26.9 ppm) for PAN.⁵ Following the same line of the above discussion of CN carbon peak, the highest magnetic field peak envelope can be assigned for the centered CH carbon of VNV triad. The difference in the chemical shifts for central CH carbon between N" N" N and VNV, both experimentally evaluated (2 ppm) should equal $2\{\omega_v + \gamma_v - (\omega + \gamma)\}$: In other words, we obtain the relation $\omega_v + \gamma_v - (\omega + \gamma) = 1$, which enables us to determine the order of the relative chemical shifts in CH carbon region of the triads. The results are: N' N' N > N' N" N > N" N" N > VN' N > VN" N > VNV from the lower magnetic field, as shown in 5th column of Table IV. These results suggest that CN and CH carbon peak regions should consist of 5 and 6 envelopes, respectively. In fact, Figure 2 clearly shows 5 envelopes for CN and 6 envelopes for CH carbon peak region. Then, the 5 envelopes for CN carbon are assigned from lower magnetic field as VNV, VN" N, VN' N + N" N" N,

$\text{N}^{\text{r}}\text{N}^{\text{m}}\text{N}$, and $\text{N}^{\text{r}}\text{N}^{\text{r}}\text{N}$ and 6 CH carbon envelopes are assigned from lower magnetic field as $\text{N}^{\text{r}}\text{N}^{\text{r}}\text{N}$, $\text{N}^{\text{r}}\text{N}^{\text{m}}\text{N}$, $\text{N}^{\text{m}}\text{N}^{\text{m}}\text{N}$, $\text{VN}^{\text{r}}\text{N}$, $\text{VN}^{\text{m}}\text{N}$, and VNV . These assignment are strictly consistent with those given by König and Wendsch,⁴ who confirmed the validity of their assignment by comparing experimental peak intensities with those calculated with 1st order Markov statistics on total triad sequence distribution and then with Bernoullian statistics on continuous N triad distribution.

The fine structure of each NMR envelope both for CN and CH carbon might come from pentad sequences adding N or V monomer unit at the both sides of the base triads shown in Table IV, as proved by our previous experimental fact⁵ that the second adjacent monomer unit do not give large influence on the chemical shifts of the CN and CH carbons in the centered monomer unit for base triads.

The relative chemical shifts of the centered CN for all the pentad sequences are listed in the 2nd column of Table II. The order of the relative chemical shifts in a group of pentad sequences originating from the same base triads is shown in the 3rd column of Table II. Here, we used the values of parameters, estimated in this paper for AN/VDC copolymer and for PAN,⁵ except for $-\sigma_{\text{nv}}$, which is evaluated to be 0.13–0.14 ppm from the difference of the experimental chemical shifts between VVNVV and NVNVV. Two groups of pentads that originated from $\text{N}^{\text{r}}\text{N}^{\text{m}}\text{N}$ and $\text{VN}^{\text{r}}\text{N}$ overlapped because the relative chemical shifts for the centered CN of the base triads are expected to be almost equivalent and the order of the relative chemical shifts expressed by parameters are given within two groups as a whole. Although 3 peaks are expected from Table II for the 4th lower magnetic field envelope (pentads from $\text{N}^{\text{r}}\text{N}^{\text{m}}\text{N}$ triad), only one peak with a shoulder is observed experimentally in Figure 2a. This might be solved by including the 3rd lower magnetic field peak ($\text{N}^{\text{r}}\text{N}^{\text{r}}\text{N}^{\text{m}}\text{N}^{\text{r}}\text{N}$) into the 2nd lower magnetic field peak groups because the probability of

the production of 5 continuous N sequence might be very small. Table II also predicts 4 peaks for the 3rd lower magnetic field envelope (pentads from $\text{N}^{\text{r}}\text{N}^{\text{m}}\text{N}$ and $\text{VN}^{\text{r}}\text{N}$) but only 3 peaks are experimentally observed in Figure 2a. Among these expected 4 peaks, the difference in relative chemical shifts between 2nd and 3rd lower magnetic field peaks is expected to be smallest and thus we can regard the 2nd and 3rd peaks as one group. A tentative (but confirmed later) peak assignment on CN carbons is indicated in Figure 2a. The corresponding peak intensities (weight fraction) is also shown in the 5th column of Table II and total weight fraction denoted as Σ means the weight fraction of the base triad.

Six carbon envelopes, corresponding to 6 base triads for CH carbon splitted mainly by addition of V monomer to the base triad because addition of N monomer unit to the base triads has been proved to have no influence on the chemical shifts of these base triads. The 2nd column of Table III summarizes the relative chemical shifts for the center CH peaks in all pentads. In order to obtain their order within a group of pentad sequences originating from the same base triad, we employed the following empirical relations:

$$\omega_{\text{nv}} = \gamma_{\text{v}}' \quad (1)$$

$$\begin{aligned} \omega_{\text{mv}} + \gamma_{\text{mv}} &= 0.05 - 0.1 \leq \gamma_{\text{v2}} \\ & (= 0.07 - 0.11) \end{aligned} \quad (2)$$

Equation 1 is derived by considering that the highest magnetic field envelope of CH carbon peaks experimentally observed has no clear fine structure, corresponding to three pentads, NVNVN, NVNVV, and VVNVV (see Figure 1) and this experimental fact can be explained only by eq 1. The right hand side of eq 2 is derived from the difference in experimental peak positions between $\text{VN}^{\text{r}}\text{N}^{\text{m}}\text{N}^{\text{m}}\text{N}$ and $\text{N}^{\text{r}}\text{N}^{\text{m}}\text{N}^{\text{m}}\text{N}^{\text{r}}\text{N}$ or $\text{VN}^{\text{r}}\text{N}^{\text{m}}\text{N}^{\text{m}}\text{NV}$ (0.05–0.10), corresponding to $\omega_{\text{mn}} + \gamma_{\text{mv}} \cdot \gamma_{\text{v2}}$ is estimated from the difference of the chemical shifts, experimentally obtained, for $\text{VN}^{\text{r}}\text{N}^{\text{r}}\text{NV}$ and $\text{N}^{\text{r}}\text{N}^{\text{r}}\text{N}^{\text{r}}\text{N}$

or VN'N'NV. When $\omega_{nv} - \gamma'_v = 0$ is considered, the 4th lower magnetic field envelope (VN'N as base triad) should have almost a single peak and the 5th lower magnetic envelope (VN''N as base triad) also should be separated into two peaks, judging from their relative chemical shifts expressed by parameters, and was actually found so experimentally, as shown in Figure 2b. The order of the relative chemical shifts from lower magnetic field within a group of pentad is shown in the 3rd column of Table III. The corresponding weight fractions of peaks are also summarized in Table III. Total weight fraction denoted as Σ means the weight fraction of the base triad. Comparison of the order given in Table III and the experimentally observed peak position enables us to give CH carbon peak assignment as shown in Figure 2b.

The peak assignment carried out here can be proved valid by comparing peak intensities for CN and CH carbon peaks. From Table II, base triad fractions determined from CN carbon peak region are: VNV, 0.124; VN''N, 0.206; VN'N + N''N''N, 0.330; N''N'N, 0.235; N'N'N, 0.105. From Table III those determined from CH carbon peak region are: VNV, 0.103; VN''N, 0.197; VN'N, 0.202; N''N''N, 0.135; N''N'N, 0.245; N'N'N, 0.117. The both results are in fairly good agreement when uncertainty in determining peak intensities of each peak is taken into consideration.

Itoh *et al.*² pointed out that the diad sequence distribution of AN/VDC copolymer was in a very good agreement with the diad sequence distribution theoretically estimated using Mayo-Lewis equation, which is derived in terms of 1st order Markov statistics. This means explicitly that stereoregularity of AN is not necessarily to be considered in the reaction of AN monomer with VDC monomer. Therefore, the assumption adopted here that VDC monomer unit interacts equally with adjacent AN monomer unit irrespective of the stereoregularity of AN monomer, is reasonable.

Figure 4. Schematic representation of the method for direct and theoretical evaluation of diad, triad, tetrad, and pentad through experimental peak fraction. Real line, directly from experimental peak fractions; dot-dash line, directly from experimental peak fractions with some exception; dotted line, theoretically from a given sequence distribution provided that the given sequence distribution is determined from experimental peak fractions.

As schematically shown in Figure 4, the sequence distributions of the diad, triad, tetrad and pentad of AN/VDC copolymer can be directly evaluated by applying the peak assignment of ^{13}C -NMR spectrum although some of them heavily overlap. Of course, assuming the polymerization mechanism, diad, triad, tetrad... sequence distributions can be indirectly calculated from the distribution of other sequences as shown in the same figure. The weight fractions of diad, triad, tetrad and pentad sequences determined either directly or indirectly in these way are given in Tables V and VI. Here, the values calculated indirectly are shown in parenthesis. Besides CH_2 carbon peak analysis, the ratio of diad distribution $F_{\text{NN}}/F_{\text{NV}}$ and $F_{\text{VV}}/F_{\text{VN}}$ can also be calculated from triad distribution (*i.e.*, F_{NNN} , F_{NNV} , F_{VNV} , F_{NVN} , F_{VVV} , and F_{VNV}) by analysis on CH and CCl_2 peaks through use of the following equations:

$$F_{\text{NN}} = F_{\text{NNN}} + 0.5F_{\text{NNV}} \quad (3a)$$

$$F_{\text{NV}} = F_{\text{VNV}} + 2F_{\text{NVN}} = F_{\text{NNV}} + 2F_{\text{VNV}} \quad (3b)$$

$$F_{\text{VV}} = F_{\text{VVV}} + 0.5F_{\text{VNV}} \quad (3c)$$

Here, the symbol denotes the fraction of the sequence shown in suffix. As shown in Table V, $F_{\text{NN}}/F_{\text{NV}}$ and $F_{\text{VV}}/F_{\text{VN}}$ values, estimated directly and indirectly, are in good agreement with each other. The monomer reactivity ratio r_{N} and r_{V} are given¹⁰ by

Table V. Diad, triad, and tetrad sequence distributions as expressed by weight fraction

Sequence		Distribution (weight fraction)			
		CH_2	CH	CN	CCl_2
Diad	NN	0.49 ₅	—	—	—
	NV	0.44 ₆	—	—	—
	VV	0.05 ₆	—	—	—
	NN/NV	1.10 ₉	(1.15 ₂) ^a	—	—
	VV/VN	0.12 ₅	—	—	(0.10 ₆) ^a
	—	—	—	—	—
Triad	NNN	(0.47 ₅) ^b	0.49 ₈	} 0.87 ₆	—
	VNN	(0.42 ₈) ^b	0.39 ₉		—
	VNV	(0.09 ₇) ^b	0.10 ₃	0.12 ₄	—
	NVN	(0.65 ₂) ^b	—	—	0.70 ₃
	VVN	(0.31 ₁) ^b	—	—	0.24 ₄
	VVV	(0.03 ₆) ^b	—	—	0.05 ₃
Tetrad	NNNN	0.24 ₅	(0.23 ₆) ^c	—	—
	VNNN	0.20 ₃	(0.21 ₂) ^c	—	—
	VNNV	0.04 ₇	(0.04 ₈) ^c	—	—
	NVNN	0.25 ₀	(0.24 ₉) ^c	—	—
	VVNN	0.16 ₇	(0.05 ₉) ^c	—	—
	VNVN	—	(0.11 ₃) ^c	—	—
	VVNV	0.02 ₉	(0.02 ₆) ^c	—	—
	NVVN	0.03 ₄	(0.03 ₄) ^c	—	—
	VVVN	0.02 ₂	(0.01 ₆) ^c	—	—
	VVVV	—	(0.00 ₁) ^c	—	—

^a Calculated from triad distribution by eq 3.^b Calculated from diad distribution by eq 11a.^c Calculated from diad distribution by eq 11b.

$$r_N = 2(F_{NN}/F_{NV})/u \quad (4)$$

$$r_V = 2(F_{VV}/F_{VN}) \cdot u \quad (5)$$

with

$$u = [M_N]/[M_V] \quad (6)$$

Here, u is the unreacted monomer ratio and $[M_N]$ and $[M_V]$ are the monomer mole concentrations, respectively. In this connection, we used the feeding monomer ratio for eq 6 because the polymerization system employed here is azeotropic either at initial or final stage of the reaction.^{1,3} In deriving eq 4 and 5 the 1st order Markov chain statistics is assumed. Then, r_N and r_V for AN/VDC copolymers can be calculated from analysis of

Table VI. Pentad sequence distributions

Sequence	Distribution		
	CH	CN	Calcd (eq 11c)
NNNNN	—	—	(0.22 ₆)
VNNNN	—	—	(0.20 ₃)
VNNNV	—	—	(0.04 ₅)
NVNNN	—	—	(0.23 ₆)
NVNNV	—	—	(0.10 ₆)
VVNNN	—	—	(0.05 ₉)
VVNNV	—	—	(0.02 ₆)
NVNVN	} 0.10 ₃	0.07 ₆	(0.06 ₁)
NVNVV		0.03 ₇	(0.03 ₀)
VVNVV		0.01 ₁	(0.00 ₄)

Table VII. Monomer reactivity ratio, r_N and r_V values estimated by CH, CH_2 , and CCl_2 carbon peak analysis

	CH	CH_2	CCl_2	A_V
r_N	0.90	0.86	—	0.88 ± 0.02
r_V	—	0.64	0.55	0.60 ± 0.05

CH and CH_2 carbon peaks and CH_2 and CCl_2 carbon peaks, respectively. The results are summarized in the 2nd to the 5th columns of Table VII. r_N values, estimated from the peaks due to two different carbons, are in approximately good coincidence with each other, but r_V values seem a little less accurate. In the last column of the table the average r_N and r_V values are compiled:

$r_N = 0.88 \pm 0.02$ and $r_V = 0.60 \pm 0.05$ are obtained.

Table VIII lists the monomer reactivity ratio r_N and r_V values for AN/VDC copolymer, reported in literature together with those obtained in the present study. The results obtained here are very consistent with those obtained by Bailey and Henrichs³ because the polymerization conditions employed are almost the same. In the homogeneous reaction systems r_N and r_V are nearly constant (0.83 and 0.58, respectively) irrespective of the literature. The r_N and r_V values obtained in the heterogeneous reaction deviate significantly ($r_N =$

Table VIII. Acrylonitrile-vinyliden chloride reactivity ratios

Solvent	Catalyst	Reaction temp/°C	Hetero- or homogeneity	Reactivity ratio			Ref
				r_N	r_V	$r_N \cdot r_V$	
None	BPO	60	Hetero	0.91	0.37	0.34	12
None	BPO	60	Hetero	0.88	0.44	0.39	2
<i>t</i> -Butanol	BPO	45	Hetero	0.41	1.20	0.49	13
Water-MeOH (30:70) ^a	Redox	40	Hetero	0.63	1.70	1.07	14
Water-EtOH (30:70) ^a	Redox	40	Hetero	0.73	1.39	1.01	14
Water- <i>n</i> -PrOH (30:70) ^a	Redox	40	Hetero	0.65	0.49	0.32	14
AcOH-water-MeOH (30:30:40) ^a	Redox	40	Hetero	0.70	1.80	1.26	14
AcOH-water-iso-AmOH (30:30:40) ^a	Redox	40	Hetero	0.44	0.40	0.18	14
Emulsion polym.	Redox	33	Hetero	0.58	0.39	0.23	15
Suspension polym.	Redox	45	Hetero			0.25	4
DMSO	AIBN	50	Homo	0.80	0.54	0.43	3
DMF	—	60	Homo	0.8	0.6	0.48	11
DMF	AIBN	50	Homo	0.88	0.60	0.53	This work

^a Volume ratio.^b MeOH, methanol; EtOH, ethanol; *n*-PrOH, *n*-propanol; iso-AmOH, isoamylalcohol.

0.41—0.91, $r_V=0.37$ —1.80). Of these results, the bulk polymerization without solvent gave an r_N value larger than that obtained for homogeneous reaction by *ca.* 0.1 and r_V value less than that obtained for the homogeneous reaction by 0.1—0.2. In the heterogeneous system using solvent r_N is smaller than those obtained for homogeneous and bulk polymerizations, but r_V changes significantly depending on the conditions. The heterogeneous system using *t*-butanol and water/alcohol (methanol, ethanol) as solvents gave $r_V > r_N$. The significant deviation of r_N and r_V for the heterogeneous reaction is a well-known phenomenon due to change in reaction phase during polymerization: for example, change in the rate of diffusion of monomer in the solvent, selective adsorption of monomer on the copolymer surface already produced, change in rate of propagation etc.

The transition probability P_{NN} , P_{VV} , P_{NV} , and P_{VN} can be calculated from r_N , r_V , and u by the relations,

$$P_{NN} = r_N \cdot u / (r_N \cdot u + 1) \quad (7)$$

$$P_{VV} = (r_V/u) / \{(r_V/u) + 1\} \quad (8)$$

$$P_{NV} = 1 / (r_N \cdot u + 1) \quad (9)$$

$$P_{VN} = 1 / \{(r_V/u) + 1\} \quad (10)$$

Putting the values of r_N , r_V , and u ($=2.57$) into the above equations, we obtained $P_{NN}=0.69$, $P_{VV}=0.19$, $P_{NV}=0.31$, and $P_{VN}=0.81$. The monomer composition F_N and F_V can be calculated through $F_N = F_{NN}/P_{NN}$ and $F_V = F_{VV}/P_{VV}$ to be 0.72 and 0.28, respectively. These values are exactly the same as determined experimentally and also almost the same as the feeding monomer molar fractions. Using F_N , F_V and the transition probability thus obtained, any triad, pentad... sequence fractions can also be calculated statistically: For example,

$$\text{Triad, } F_{NNN} = F_N(P_{NN})^2 \quad (11a)$$

$$\text{Tetrad, } F_{NNNV} = F_N(P_{NN})^2 P_{NV} \quad (11b)$$

$$\text{Pentad, } F_{VVNVN} = F_V P_{VV} P_{VN} P_{NV} P_{VN} \quad (11c)$$

$$F_{NVNVV} = F_N P_{NV} P_{VN} P_{NV} P_{VV} \quad (11c)$$

The results are collected in Tables V and VI in parenthesis. Excellent agreement of triad and tetrad sequences calculated with these directly determined indicate explicitly that sequence distribution of AN/VDC copolymer chain can

be very reasonably explained in terms of 1st order Markov statistics. From eq 11c we can calculate the pentad sequence distribution, when AN monomer configuration is neglected. The results are summarized in Table VI. Unfortunately, we cannot compare these with experimentally determined weight fractions either from CH or CN carbon peak intensities due to unignorable peak overlapping.

It seems very important to decide the mechanism governing the configurational characteristics of the AN sequence part of the chain. Since two CN carbon peak envelopes assigned to $\text{N}^m\text{N}^m\text{N}$ and VN^rN overlap, we evaluated these fractions by analysis on CH peaks, as listed in Table IX. When the sequence distribution is expressed by Bernoullian statistics, the probability of *meso* arrangement P_m can be estimated from the fractions of triads by the relations:

$$F_{\text{N}^m\text{N}^m\text{N}} = P_m^2 \quad (12a)$$

$$F_{\text{N}^m\text{N}^r\text{N}} = 2P_m(1 - P_m) \quad (12b)$$

$$F_{\text{N}^r\text{N}^r\text{N}} = (1 - P_m)^2 \quad (12c)$$

P_m values obtained by eq 12a—12c are collected in the 3rd column of Table IX. If the stereoregularity of AN sequence is governed by Bernoullian statistics, P_m calculated by eq 12a—12c should be the same. The results agree with what the statistics predict and $P_m = 0.52$ was obtained. Now, we can estimate all possible pentad sequence distributions where the stereoregularity of AN monomer is considered, through relations, such as

$$F_{\text{N}^m\text{N}^m\text{N}^m\text{N}^m\text{N}} = F_{\text{N}^m\text{N}^m\text{N}} \cdot P_m^4 \quad (13a)$$

$$F_{\text{N}^m\text{N}^m\text{N}^m\text{N}^r\text{N}} = F_{\text{N}^m\text{N}^m\text{N}} \cdot 2P_m^3(1 - P_m) \quad (13b)$$

$$F_{\text{N}^r\text{N}^m\text{N}^m\text{N}^r\text{N}} = F_{\text{N}^m\text{N}^m\text{N}} \cdot P_m^2(1 - P_m)^2 \quad (13c)$$

These pentad sequence distributions calculated from the equations including eq 13a—13c are summarized in the 6th column of Tables II and III. These tables enable us to judge whether our pentad peak assignments based on the electro-magnetical influence on centered CN

Table IX. NNN triad distribution of an AN/VDC copolymer sample

Sequence	Fraction (experimental) ^a	P_m
$\text{N}^m\text{N}^m\text{N}$	0.27 ₁	0.52
$\text{N}^m\text{N}^r\text{N}$	0.49 ₄	0.55
$\text{N}^r\text{N}^r\text{N}$	0.23 ₅	0.51
		-----
		av. 0.52

^a From CH peaks.

and CH carbons is reasonable. Experimental weight fractions of peaks and the corresponding theoretical grouped peak fractions are in an excellent agreement with each other. This strongly suggests that the peak assignment given here is quite reasonable.

Summarizing, we gave a rather tentative assignment of CN and CH carbon peaks in an AN/VDC copolymer based on pentad sequence distribution by considering the stereoregularity of AN monomer. For this purpose, electro-magnetical influence on the centered CN and CH carbon are taken into consideration by introducing the interaction of AN monomer with the adjacent VDC monomer. The assignment given here was proved to be reasonable if 1st order Markov statistics is first assumed on pentad distribution obtained by neglecting the stereoregularity of AN and then, Bernoullian statistics is assumed for the continuous AN monomer sequence part describing the stereoregularity. Comparison between any theoretical and experimental diad, triad, and tetrad sequence distributions also confirmed the above mechanism which has been proposed by other authors.

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