by Milton Marks of Dow's Computations Laboratory is also appreciated.

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Polymerization Modes of Tetracyanoquinodimethane and Vinyloxy Compounds

Shouji Iwatsuki* and Takahito Itoh

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464 Japan. *Received July 20, 1978*

ABSTRACT: Polymerization of tetracyanoquinodimethane (TCNQ) with *n*-butyl vinyl ether, isobutyl vinyl ether, 2-chloroethyl vinyl ether, phenyl vinyl ether, and vinyl acetate was studied in acetonitrile. The first two vinyl ethers homopolymerize in the presence of TCNQ and the last three compounds copolymerize in an alternating fashion with TCNQ. The two polymerization modes were correlated to electron-donating character of the monomers by Taft's substituent constants for vinyloxy compounds.

It has been pointed out that tetracyanoquinodimethane (TCNQ) can participate in radical copolymerizations as an acceptor monomer, causing a spontaneous alternating copolymerization with styrene (St).[1] On the other hand, Stille et al.[2] reported that TCNQ initiates the cationic homopolymerization of alkyl vinyl ethers in acetonitrile, indicating the powerful electron-accepting character of TCNQ. It was thus conceivable that the system composed of TCNQ and a donor monomer could change in its polymerization behavior from alternating copolymerization to cationic homopolymerization of the electron-donating monomer, as a function of the electron-donating character of the monomer.

The polymerization of TCNQ with *n*-butyl vinyl ether (nBVE), isobutyl vinyl ether (iBVE), 2-chloroethyl vinyl ether (CEVE), phenyl vinyl ether (PhVE), and vinyl acetate (VAc) was studied. The polymerization modes observed can be correlated with the electron-donating character of the vinyloxy compounds.

Experimental Section

1. Material. Commercial TCNQ was purified by recrystallization from acetonitrile and was sublimed (twice) (mp 294.5–295.5 °C). PhVE was prepared from phenol and dibromoethane according to the method of McElvain et al.[3] (bp 54 °C (17 mmHg)). CEVE (bp 109 °C), VAc (bp 71.0 °C), iBVE (bp 82 °C), and nBVE (bp 94.5 °C) were purified from commercial products by conventional methods.[4] The monomer purity was checked by gas chromatography (purity, 99.6–99.8%). α,α′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. Acetonitrile was refluxed with phosphorus pentoxide and then distilled at 82 °C. Dichloromethane was refluxed with calcium hydride and distilled at 39.5 °C. Boron trifluoride etherate was distilled at 125.5 °C under nitrogen.

2. Polymerization Procedure. TCNQ–iBVE and TCNQ–nBVE. TCNQ (0.1 g) and 1.0 g of iBVE (or 1.0 g of nBVE), 6.8 mg of AIBN (or 5.7 mg of AIBN for the TCNQ–nBVE system), and 10 mL of acetonitrile were placed in an ampule, which was then degassed (freeze–thaw cycle repeated three times) and sealed. The ampule was placed in a bath at 60 °C for 21.8 h (or 18.1 h for the TCNQ–nBVE system), cooled, and opened. The reaction solution was poured into excess methanol. The polymeric product was collected by filtration, dissolved in benzene, and reprecipitated in excess methanol. The yield of polymeric product was 166 mg (or 98 mg for the TCNQ–nBVE system). Anal. For the TCNQ–iBVE system Calcd for $C_6H_{12}O$: C, 71.94; H, 12.08. Found: N, 0; C, 72.34; H, 11.35. For the TCNQ–nBVE system Calcd for $C_6H_{12}O$: C, 71.94; H, 12.08. Found: N, 0; C, 72.39; H, 11.68. The solution viscosity of these products in benzene was determined at 30 °C to be $\eta_{sp/c}$ = 0.067 dL/g (*c* 2.79 g/dL) for the product of the TCNQ–iBVE system and $\eta_{sp/c}$ = 0.062 dL/g (*c* 1.15 g/dL) for that of the TCNQ–nBVE system.

TCNQ–CEVE. Given amounts of TCNQ, CEVE, and AIBN and 10 mL of acetonitrile were placed in an ampule, which was then degassed as above and sealed. The ampule was heated at

*Address correspondence to this author at the Department of Chemical Research for Resources, Faculty of Engineering, Mie University, Kamihama-cho, Tsu, 514 Japan.

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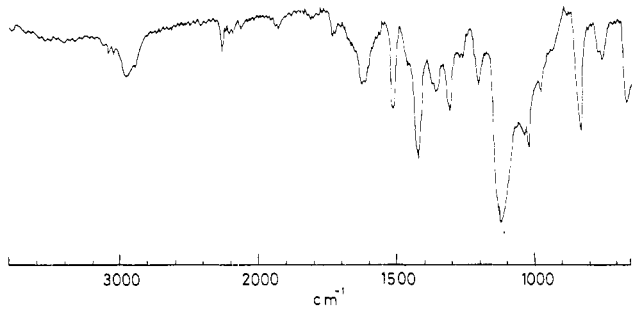

Figure 1. The IR spectrum of TCNQ–CEVE copolymer (KBr disk).

50 or 60 °C for the time of polymerization. The reaction solution was poured into excess diethyl ether and the polymeric product was collected by filteration and washed repeatedly with diethyl ether and dried under reduced pressure.

TCNQ–PhVE and TCNQ–VAc. Given amounts of TCNQ, PhVE (or VAc), and AIBN, and 10 mL of acetonitrile, were polymerized as above at 60 °C for the time of polymerization. The reaction solution was poured into excess methanol containing calcium nitrate and the polymeric product was washed well with methanol and dried under reduced pressure.

Homopolymerization of CEVE with Boron Trifluoride Etherate. Dichloromethane, 100 mL, and 10 mL of CEVE were placed under nitrogen in a 200-mL flask cooled in dry ice–methanol. About 0.26 g of BF_3·Et_2O was introduced with a syringe into the flask which was kept at −78 °C for 1 h. Diethylamine, 0.5 mL, was added to stop the polymerization. The resulting solution was poured into excess diethyl ether to precipitate a pale yellow rubbery material. The product was dissolved in dichloromethane and poured into excess methanol cooled at about 0 °C. The precipitate was dried under reduced pressure to constant weight. The yield was 5.15 g. Anal. Calcd for C_4H_7OCl: C, 45.09; H, 6.63; Cl, 33.27. Found: C, 44.38; H, 6.47; Cl, 33.19.

3. Polymer Characterization. Composition of the polymers was established by elemental analysis. ^1H NMR measurements of polymers were carried out in dimethyl-d_6 sulfoxide (Me_2SO-d_6) with tetramethylsilane (Me_4Si) as an internal standard. The solution viscosity of copolymers was determined at 30 °C with an Ubbelohde viscometer, using acetonitrile for TCNQ–CEVE copolymer and *N,N*-dimethylformamide (DMF) for TCNQ–PhVE and TCNQ–VAc copolymers as solvents.

4. Instruments for Measurement. A Yanagimoto microdetermination apparatus Model MX-3 was used for elemental analysis. A JEOL JNM-PMX 60 and a JASCO IRA-I were used for NMR and IR spectral determinations, respectively.

Results

TCNQ–iBVE and TCNQ–nBVE. Pale yellow color developed immediately when TCNQ was mixed with iBVE (or nBVE) in acetonitrile. Experiments in both systems were carried out in the presence of undissolved TCNQ. A viscous milky material was observed to form in the neighborhood of the TCNQ crystals after half an hour. The TCNQ remained almost unchanged even after 1 day. The IR spectra of polymeric products from both systems have no absorption characteristic of a nitrile group. Compositions of these polymeric products correspond well with the calculated values for the homopolymer of iBVE (or nBVE). It was concluded, therefore, that the polymeric products obtained from TCNQ–iBVE and TCNQ–nBVE systems are homopolymers of the respective vinyl ethers which polymerize cationically as reported by Stille et al.[2]

TCNQ–CEVE. Pale yellow color developed immediately when TCNQ was mixed with CEVE in acetonitrile. Experiments were carried out in the presence of undissolved TCNQ. On standing eventually all the TCNQ dissolved and the color of the solution changed to pale yellow-green. The product was obtained as a pale brown powder which was soluble at room temperature in acetonitrile, acetone, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO). In Table I the results of copolymerization of TCNQ with CEVE are summarized. It is obvious from the copolymer composition that the copolymer is composed of equimolar amounts of both monomer units.

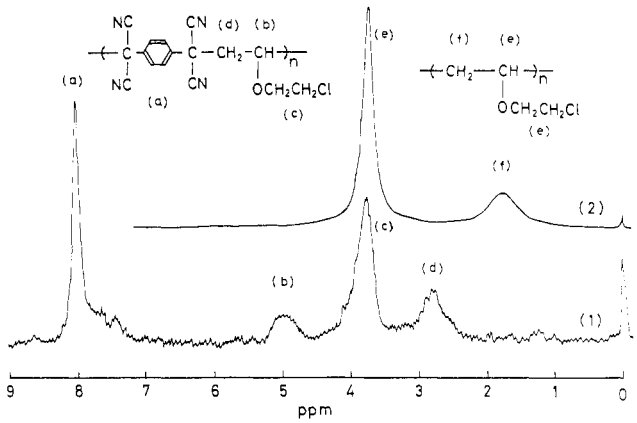

Figure 2. The NMR spectra of TCNQ–CEVE copolymer (1) and of CEVE homopolymer (2) (in Me_2SO-d_6).

In Figure 1 the IR spectrum of this copolymer is shown; absorptions were observed at 2260 cm^{-1} for a nitrile group, 1620 and 1510 cm^{-1} for an aromatic carbon–carbon double bond, and 1120 cm^{-1} for an ether group, indicating incorporation of TCNQ and CEVE units into the copolymer. In Figure 2 are shown NMR spectra for the copolymer and for the homopolymer of CEVE prepared with BF_3·Et_2O. The copolymer has four absorptions which appear at 8, 5, 3.8, and 2.8 ppm. The resonances at 8 and 3.8 ppm are assigned to the phenylene protons of a TCNQ unit and to the ethylene protons of a 2-chloroethyloxy group in a CEVE unit, respectively. Absorptions at 5 and 2.8 ppm are attributed to methine and methylene protons of a CEVE unit in the main chain, respectively. In the homopolymer, two absorptions appear at 3.8 and 1.7 ppm. The absorption at 3.8 ppm is assigned to a methine proton of the main chain and also to the side-chain protons of a 2-chloroethyloxy group. The resonance at 1.7 ppm is assigned to methylene protons of a CEVE unit in the main chain. Apparently, methine and methylene protons of a CEVE unit in a copolymer are much more subject to deshielding than the corresponding protons in a homopolymer of CEVE; similar behavior was observed for protons of the donor monomer unit in alternating copolymers between TCNQ and St[1] and between $\alpha,\alpha,\alpha',\alpha'$,2,5-hexachloro-*p*-xylylene and St.[5] The deshielding could arise from the powerful electron-withdrawing effect of the neighboring dicyanomethylene groups of TCNQ units in the copolymer. It can therefore be concluded that the copolymer of TCNQ with CEVE is really alternating.

TCNQ–VAc. The variation in color and state of the reaction mixture during the reaction for polymerization of the TCNQ–VAc system was similar to the TCNQ–CEVE system. The product was obtained as a pale green powder which was insoluble at room temperature in benzene, chloroform, and acetonitrile, but was soluble at room temperature in aprotic polar solvent such as DMF and Me_2SO. In Table II the results of the copolymerization of TCNQ with VAc are summarized. It is evident from the composition that the copolymers are composed of equimolar amounts of both monomer units, independently of monomer feed ratio.

In Figure 3 an NMR spectrum of the copolymer (TA-2) is shown; four absorptions at 8, 5.8, 3.4, and 2.1 ppm can definitely be assigned as the phenylene protons of the

Table I
Polymerization Results for the TCNQ–CEVE System[a]

run no.	monomer feed		TCNQ, mol %	polymn time, h	AIBN, mg	polym yield, mg	conv, %	copolymer composition[b]					
	TCNQ, g	CEVE, g						elemental anal.				TCNQ, mol %	$\eta_{sp/c}$,[c] dL/g
								N	C	H	Cl		
T.C-1	0.103	1.040	4.9	17.7	0	46.0	4.0	17.26	61.44	4.01	11.98	47.6	0.449
T.C-2	0.100	1.036	4.8	22.0	9.5	52.2	4.6	16.22	59.99	4.05	12.71	44.0	
T.C-3	0.110	1.039	5.2	22.0	0	54.0	4.7	16.29	60.22	4.00	12.68	44.0	

[a] Solvent: 10 mL of acetonitrile. Temperature of polymerization: 50 °C (T.C-1) and 60 °C (T.C-2 and -3). [b] Calculated values for the copolymer of 1:1 TCNQ and CEVE unit: C, 61.84; H, 3.57; N, 18.03; Cl, 11.41. [c] Solvent: acetonitrile. Temperature: 30 °C.

Table II
Polymerization Results for the TCNQ–VAc System[a]

run no.	monomer feed		TCNQ, mol %	AIBN, mg	polymn time, h	polym yield, mg	conv, %	copolymer composition[b]				
	TCNQ, g	VAc, g						elemental anal.			TCNQ, mol %	$\eta_{sp/c}$,[c] dL/g
								N	C	H		
T.A-1	0.099	1.006	4.0	6.6	20.5	52.7	4.8	18.20	65.76	3.79	46.1	
T.A-2	0.172	0.633	10.3	10.0	46	154.1	19.2	18.38	65.30	3.67	46.5	0.098
T.A-3	0.201	0.254	25.0	5.2	49.5	18.9	4.2	18.71	65.41	3.75	47.2	

[a] Solvent: 10 mL acetonitrile. Temperature of polymerization: 60 °C. [b] Calculated values for the copolymer of 1:1 TCNQ and VAc unit: C, 66.20; H, 3.47; N, 19.30. [c] Solvent: DMF. Temperature: 30 °C.

Table III
Polymerization Results for the TCNQ–PhVE System[a]

run no.	monomer feed		TCNQ, mol %	AIBN, mg	polymn time, h	polym yield, mg	conv, %	copolymer composition[b]				
	TCNQ, g	PhVE, g						elemental analysis			TCNQ, mol %	$\eta_{sp/c}$,[c] dL/g
								N	C	H		
T.P-1	0.110	1.053	5.8	5.5	21.6	135.0	11.6	17.01	72.82	4.32	49.0	0.135
T.P-2	0.202	0.312	17.6	5.7	25.8	97.6	19.0	16.95	72.33	4.19	48.7	
T.P-3	0.202	0.175	40.5	5.6	40.8	108.8	28.9	16.23	73.21	4.14	47.9	
T.P-4	0.101	0.966	5.4	0.0	48.5	148.9	13.9	16.50	73.36	4.20	47.0	

[a] Solvent: 10 mL of acetonitrile. Temperature of polymerization: 60 °C. [b] Calculated values for the copolymer of 1:1 TCNQ and PhVE unit: C, 74.06; H, 3.73, N, 17.28. [c] Solvent: DMF. Temperature: 30 °C.

Table IV
Taft's and Hammett's Substituent Constants of Vinyloxy and Vinyl Compounds

vinyloxy compd				vinyl compounds			
substituents R	Taft's constant[8] σ^*	Hammett's constant σ_m	Hammett's constant σ_p	substituents R′	Hammett's constant σ_m	Hammett's constant σ_p	e value[17]
CH_3CO	+1.65	+0.376[14]	+0.502[14]	CH_3COO	+0.39[14]	+0.31[14]	−0.220
C_6H_5	+0.600	+0.06[14]	−0.01[14]	C_6H_5O	+0.25[14]	−0.32[14]	−1.210
$ClCH_2CH_2$	+0.385		(+0.18[16])[a]				−1.41[12]
C_2H_5	−0.100	−0.07[14]	−0.151[14]	C_2H_5O	+0.1[14]	−0.24[14]	−1.170
n-C_3H_7	−0.115	−0.05[15]	−0.126[15]	n-C_3H_7O	+0.1[14]	−0.25[14]	−1.520
i-C_3H_9	−0.125		−0.115[16]				−1.770
n-C_4H_9	−0.130	−0.07[15]	−0.161[15]	n-C_4H_9O	+0.1[14]	−0.32[14]	−1.200
i-C_3H_7	−0.190	−0.07[15]	−0.151[14]	i-C_3H_7O	+0.1[14]	−0.45[14]	−1.310
t-C_4H_7	−0.300	−0.10[14]	−0.197[14]				−1.580

[a] Value for $ClCH_2$.

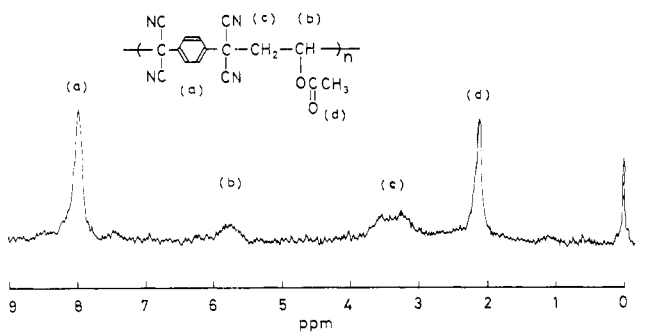

Figure 3. The NMR spectrum of TCNQ–VAc copolymer (in Me_2SO-d_6).

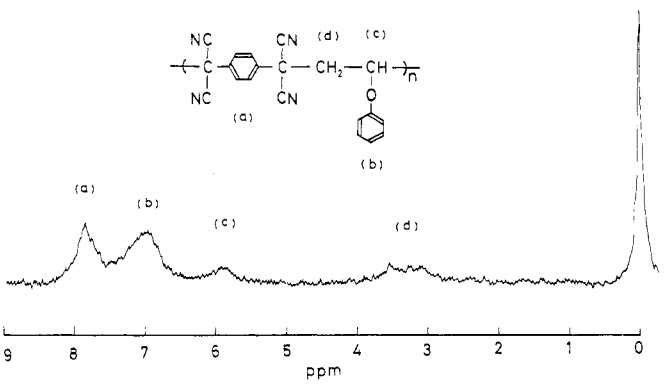

Figure 4. The NMR spectrum of TCNQ–PhVE copolymer (in Me_2SO-d_6).

TCNQ unit and the methine, methylene, and acetyl protons of a VAc unit, respectively. On the other hand, the homopolymer of VAc[6] was reported to have three kinds of NMR absorptions at 4.8 (methine), 2.0 (acetyl), and 1.8 ppm (methylene). Accordingly, the methine and methylene protons of VAc unit in this copolymer are also observed at a lower field than for the homopolymer of VAc. Therefore, it is also concluded that the copolymer of TCNQ with VAc is really alternating.

TCNQ–PhVE. The variation in color and state of the reaction mixture for the TCNQ–PhVE polymerization system and the solubility of the product were similar to the TCNQ–VAc system. The product was obtained as a pale brown powder. In Table III the results of the copolymerization of TCNQ with PhVE are summarized. It is obvious from the copolymer composition that the copolymers are composed of equimolar contents of both monomer units, independent of monomer feed ratio.

In Figure 4 is shown an NMR spectrum of the copolymer. The absorptions at 7.8, 7, 6, and 3.2 ppm can be assigned to the phenylene protons of a TCNQ unit, the phenyl protons of a PhVE unit, and to the methine and methylene protons of a PhVE unit, respectively. The positions of the resonances for the methine and methylene protons of a PhVE unit of the copolymer are in reasonable agreement with the behavior of donor units of the above-mentioned alternating copolymers between TCNQ and CEVE, and between TCNQ and VAc. Therefore this copolymer is also concluded to be really alternating.

Discussion

It is thus sure that TCNQ–CEVE, TCNQ–VAc, and TCNQ–PhVE give alternating copolymers, whereas TCNQ–iBVE and TCNQ–nBVE only homopolymerize to poly(vinyl ethers). These two polymerization modes, including the data of Stille et al.,[2] can be correlated with the electron-donating character of the donor monomer in a quantitative sense. The indices employed for the electron-donating character were Hammett's[7] and Taft's[8] substituent constants either for vinyloxy compounds or for vinyl compounds and also the e value of the Q–e scheme of Alfrey and Price.[9] It is obvious in Table IV that the polymerization modes can be classified without exception when the donor monomers are arranged in order of magnitude of Taft's substituent constants, σ^*, for vinyloxy compounds, CH_2=CHOR. Of course, taking into account the reacting position of the monomer, the substituent constants for vinyl compounds, CH_2=CHR′, would be better choices than those for the vinyloxy compounds. However, the relatively large number of known substituent constants and the wide range of a substituent constant with a variety of substituents forced us to use Taft's values for the vinyloxy compounds. Interestingly, the substituent constants apparently suitable for this classification, such as Taft's σ^* and Hammett's σ_m for vinyloxy compounds and Hammett's σ_m for vinyl compounds, are known as polar substituent parameters exclusive of resonance. An insufficient separation between polar and resonance terms in e values may be related to some discrepancies between these e values and our classification. It is here to be borne in mind that the Q–e scheme is recognized as an empirical or a quasitheoretical correlation and that the e value is a crude indication of the polar effect. Moreover, e values for vinyl ethers should be considered to contain large uncertainties because of their very poor homopolymerizability and copolymerizability via radical mechanisms.

It can further be pointed out that vinyloxy compounds with a substituent of a positive Taft's σ^* value copolymerize alternatingly with TCNQ and those of a negative σ^* value homopolymerize cationically. This observation suggests the conjecture that an electron transfer reaction between vinyloxy compound and TCNQ takes place to yield an amount of a cationic species[2,10] which initiates cationic polymerization if the inductive

effect of the substituent in the vinyloxy compound is stronger than a limiting value. Vinyloxy compounds with electron-donating character weaker than this value interact with TCNQ to form, exclusively, a charge-transfer complex which plays an important role in their alternating copolymerization. It is impossible to exclude definitely the possibility that cationic polymerization of the vinyl ethers studied here is caused by an unknown acidic contaminant in TCNQ (as was reported for tricyanoethenol in tetracyanoethylene[11]), even though TCNQ was purified as well as possible. However, the alternating copolymerizations are not affected by such an impurity even if it is contained in TCNQ. When maleic anhydride with much weaker electron-accepting character (EA = 0.11 eV)[12] is used in place of TCNQ (EA = 1.7 eV)[12], alkyl vinyl ethers do not homopolymerize at all but they still copolymerize alternatingly.[13] It is concluded, therefore, that balance between electron-donating and electron-accepting character of both monomers is a primary determining factor of the polymerization modes.

It is apparent from the results in the tables that alternating copolymerizations of TCNQ with CEVE and PhVE take place even in the absence of AIBN. It is also to be noted that in at least one instance (TA-2) AIBN markedly enhances the yield of polymer. These unusual effects cannot be discussed at this time in a meaningful way because the system is inhomogeneous except at very dilute concentrations of TCNQ. Further work to clarify these effects as well as the influence of solvent on the polymerization is currently in progress.

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Poly(2,3-epoxybutanes) and Poly(1,4-dichloro-2,3-epoxybutanes): Microstructure and Mechanism of Polymerization Studied by Carbon-13 Magnetic Resonance Spectroscopy†

Floyd F.-L. Ho* and E. J. Vandenberg

Research Center, Hercules Incorporated, Wilmington, Delaware 19899.

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ABSTRACT: Carbon-13 magnetic resonance (^{13}C NMR) spectra of meso and racemic 2,3-epoxybutanes and the related dimer and trimer fractions were obtained. These compounds were used as models to aid in assigning ^{13}C NMR signals from crystalline poly(2,3-epoxybutane)'s and poly(1,4-dichloro-2,3-epoxybutanes). Crystalline poly(*cis*-2,3-epoxybutane) and poly(*cis*-1,4-dichloro-2,3-epoxybutane) were found to have predominantly racemic triads (e.g., -RR-RR-RR-), while crystalline poly(*trans*-2,3-epoxybutane) and poly(*trans*-1,4-dichloro-2,3-epoxybutane) were found to have stereoblocks with -RS-RS-RS- (or -SR-SR-SR-) and -RS-RS-SR- (or -SR-SR-RS-) triad arrangements. The average sequence length of a block is approximately five units long (i.e., -RS-RS-RS-RS-RS-SR-SR-SR-SR-SR-). A mechanism of polymerization with exclusive inversion of configuration at the epoxide ring-opening carbon, first proposed by Vandenberg in 1961, was further confirmed by this work. Some degree of enantiomorphic selection in the polymerization of racemic *trans*-2,3-epoxybutane was also indicated.

In previous work on 2,3-epoxybutane polymerization, Vandenberg[1] demonstrated that polymerization of epoxides proceeds with clean inversion of configuration at the ring-opening carbon atom. This conclusion was based largely on the detailed analyses of dimer and trimer diols from cleavage studies on the polymer. This paper reports our recent investigation using carbon-13 magnetic resonance (^{13}C NMR) spectroscopy.

^{13}C NMR has been shown to be a powerful tool for studies of the microstructure of polymer.[2,3] In the case of polyethers, ^{13}C NMR studies have been reported on poly(ethylene oxide),[4,5] poly(propylene oxide),[6-8] and ethylene oxide–propylene oxide copolymers,[5] among

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