(15) Becker, E. D. "High Resolution NMR; Theory and Chemical Applications", 2nd ed.; Academic Press: New York, 1980.
(16) Overman, L. E.; Freerks, R. L.; Petty, C. B.; Clizbe, L. A.; Ono, R. K.; Taylor, G. F.; Jessup, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2816.
(17) Semmelhack, M. F.; Tomoda, S.; Hurst, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 7567.
(18) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 3rd ed.; Wiley: New York, 1974.
(19) Grieco, P. A.; Ferrino, S.; Giovanni, V. *J. Am. Chem. Soc.* **1980**, *102*, 7586.
(20) Field, N. D.; Lorenz, D. H. In "Vinyl and Diene Monomers, Part 1"; Leonard, E. C., Ed.; Wiley-Interscience: New York, 1970.
(21) Ischihara, A.; Kimura, R.; Moriyasu, K.; Sakamura, S. *Tetrahedron Lett.* **1977**, 4331.
(22) Taskinen, E.; Mukkala, V.-M. *Tetrahedron* **1982**, *18*, 613.
(23) Flitsch, W.; Kappenberg, F. *Chem. Ber.* **1978**, *111*, 2396.
(24) Huckel, W.; Muller, H. *Ber.* **1931**, *64*, 1981.

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# Stereochemical Evidence for Participation of a Donor–Acceptor Complex in Alternating Copolymerization. 2. Copolymer Structure

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ABSTRACT: Various N-substituted maleimides have been shown to alternately copolymerize with several vinyl ethers. The stereochemistry of these copolymers, as deduced from $^{13}$C NMR spectroscopy, is markedly dependent on such copolymerization conditions as temperature, solvent, total monomer concentration ($M_T$), comonomer concentration ratio at fixed total monomer concentration, and the donor–acceptor character of the comonomer pair. Copolymerization conditions favoring the formation of a comonomer donor–acceptor complex (DA) invariably gave higher cis:trans stereochemical ratios at the succinimide units in the resulting copolymers. The results are interpreted as indicating that copolymer succinimide unit stereochemistry is dependent on the fraction of maleimide monomer in complex form and that the DA participates significantly in the propagation steps of the copolymerization.

## Introduction

The question of participation of a donor–acceptor complex (DA) in alternating copolymerizations has long been debated. Bartlett and Nozaki[2] first proposed such participation as an explanation for the alternating nature of some copolymers as early as 1946. Walling et al.[3] postulated that the observed alternation resulted from a lowering of the activation energy for cross propagation reactions relative to homopropagations due to polarity differences between the radical chain end and the incoming monomer. Tsuchida and Tomono[4] introduced the concept that both "free" and "complexed" comonomers may participate in alternating copolymerizations. Methods have recently been developed which utilize kinetic[5,6] data in order to quantify the extent of DA participation in copolymerizations. Better fits to copolymer composition[7-9] and triad fraction[10] data have been obtained by invoking kinetic schemes that include participation of DA in copolymerization propagation steps. In spite of the large amount of data (especially composition data) that has been amassed over the years, several authors[11,12] have suggested that there has been no unambiguous experimental proof of any of the above mechanisms. This could be due to errors inherent in the determination of copolymer compositions, triad fractions, and copolymerization rates, or due to the fact that assumptions of relative values of certain rate constants are often made in these kinetic analyses. Thus, in order to clarify the mechanism of alternating copolymerization, a new source of data was deemed necessary.

Mulliken theory[13] predicts that the maximum amount of charge-transfer stabilization is to be expected if a complex adopts a conformation in which there is maximum overlap between the HOMO of the donor and the LUMO of the acceptor. It is therefore conceivable that if a DA adds to the radical chain end in a concerted manner (as opposed to a stepwise addition of the complex components), then a certain amount of stereoregularity may be induced into the copolymer chain. The degree of stereoregularity may be related to the amount of complex participation in the propagation steps.

In this paper, we show that the appearance of the $^{13}$C NMR spectra of certain alternating copolymers of N-substituted maleimides and vinyl ethers varies with the copolymerization conditions. The changes in the $^{13}$C NMR spectra are shown to be due to stereochemical differences in the copolymers. Copolymerization conditions that favored the formation of a DA invariably resulted in more stereoregular copolymers. Some of these results have been previously reported.[14] We now report the details of this study.

## Experimental Section

**General.** All temperatures are uncorrected and are reported in degrees centigrade. Melting points were determined in open capillary tubes using a Thomas-Hoover melting point apparatus.

Infrared (IR) spectra were obtained by using a Perkin-Elmer Model 281 infrared spectrophotometer. Vibrational transition frequencies are expressed in wavenumbers (cm$^{-1}$), with bands being assigned the following classifications: weak (w), medium (m), strong (s), very strong (vs), and broad (b). Proton nuclear magnetic resonance (NMR) spectra (60 MHz) were obtained on either a Varian A-60A or a Jeol JNM-PMX-60 spectrometer. Carbon-13 (25.00 MHz) and 100-MHz proton NMR spectra were recorded on a Jeol JNM-FX-100 instrument. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane unless stated otherwise. Multiplicities of proton-decoupled and off-resonance-decoupled $^{13}$C resonances are des-

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ignated as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). Coupling constants (*J*) are expressed in hertz (Hz). Mass spectra [low resolution (LRMS)] were recorded on an Associated Electronics Industries (AEI) Model MS-30 spectrometer. Ultraviolet (UV) spectra were run on a Beckman ACTA V spectrophotometer. Polymer number-average molecular weights ($M_n$) were determined with a Wescan 233 molecular weight apparatus (vapor pressure osmometer). Chemical analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Unless otherwise noted, reagents were obtained from Aldrich Chemical Co. Dichloromethane ($CH_2Cl_2$) was distilled from $P_4O_{10}$ immediately before use. Purifications of other solvents were carried out by using standard procedures[15] and are described in the text. Deuterated solvents [chloroform-*d* ($CDCl_3$), acetone-$d_6$, dimethyl-$d_6$ sulfoxide ($Me_2SO$-$d_6$), and dichloromethane-$d_2$ ($CD_2Cl_2$)] for NMR spectra were obtained from either Merck and Co., Inc., Stohler Isotope Chemicals, or Aldrich Chemical Co. and were used without further purification. *N*-Phenylmaleimide was obtained from Aldrich Chemical Co. and was recrystallized from cyclohexane before use.

**Maleimide Synthesis. General.** Many of the maleimides used in this study [*N*-(4-fluorophenyl), *N*-(4-chlorophenyl), *N*-(4-bromophenyl), *N*-(4-nitrophenyl), *N*-(4-carbethoxyphenyl), *N*-(4-methylphenyl), *N*-(4-acetoxyphenyl), and *N*-(4-methoxyphenyl)] had been previously synthesized in these laboratories.[16] They were purified by recrystallization from cyclohexane and characterized by various spectral techniques. Only the spectral data for these maleimides are given here. The *N*-acetoxymaleimide used was synthesized in these laboratories[17] and was used without further purification.

In general, the synthetic procedure first developed by Searle[18] and detailed by Barrales-Rienda et al.[19] was used. The procedure involved the reaction of the appropriately substituted aniline with maleic anhydride to form an intermediate maleanilic acid. The maleanilic acid is then dehydrated to the maleimide using acetic anhydride–sodium acetate. The following maleimides, along with intermediates, yields, melting points, and literature references, were prepared for this study:

***N*-Cyclohexylmaleanilic acid [4-(cyclohexylamino)-4-oxo-(*Z*)-2-butenoic acid] (1)**: yield, ~100%; mp 153–154 °C (lit.[20] mp 182 °C).

***N*-Cyclohexylmaleimide (1-cyclohexyl-1*H*-pyrrole-2,5-dione)[21] (2)**: yield, 22% (based on recovered starting material); mp 86–87 °C (lit.[22] mp 89 °C).

$^{13}C$ NMR ($CDCl_3$) $\delta$ 25.10, 25.98, 29.95, 50.74, 133.91, 170.85.

***N*-(4-(Trifluoromethyl)phenyl)maleamic acid (4-oxo-4-[(4-(trifluoromethyl)phenyl)amino]-(*Z*)-2-butenoic acid) (3)**: yield, 95.2%; mp 183–184 °C (lit.[23] mp 183–186 °C).

***N*-(4-(Trifluoromethyl)phenyl)maleimide [1-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-2,5-dione] (4)**: yield, 86.0%; mp 153–155 °C (lit.[23] mp 150–152 °C).

$^{13}C$ NMR (acetone-$d_6$, letters denote actual multiplicities, *J*'s are $^{13}C$–$^{19}F$ coupling constants in hertz) $\delta$ 125.03 (q, $J = 271.0$), 126.90 (q, $J = 3.7$), 127.52 (s), 129.40 (q, $J = 33.0$), 135.74 (s), 136.49 (s), 170.02 (s). Off-resonance decoupling caused all peaks to split into doublets, relative to the completely decoupled spectrum, except for those at 125.03, 129.40, 136.49, and 170.02, which remained singlets. Selective irradiation of the ethylenic protons resulted in a much greater intensity for the $^{13}C$ peak at 135.74, relative to the other carbon resonances.

$^{13}C$ NMR ($CDCl_3$) $\delta$ 123.82 (q, $J = 272.2$), 125.79 (s), 126.26 (q, $J = 3.7$), 129.64 (q, $J = 33.0$), 134.42 (s), 134.59 (s), 168.92 (s).

***N*-(4-Cyanophenyl)maleamic acid (4-[(4-cyanophenyl)amino]-4-oxo-(*Z*)-2-butenoic acid) (5)**: yield, 93.4%; mp 193–194 °C.

$^{13}C$ NMR ($Me_2SO$-$d_6$, internal reference[24] $Me_2SO$-$d_6$ = 39.5) $\delta$ 105.47, 118.65, 119.48, 129.76, 131.93, 132.93, 142.65, 163.78, 166.29.

***N*-(4-Cyanophenyl)maleimide [1-(4-cyanophenyl)-1*H*-pyrrole-2,5-dione] (6)**: yield, 81.2%; mp 131–134 °C.

$^{13}C$ NMR ($CDCl_3$) $\delta$ 110.98 (s), 118.16 (s), 125.69 (d), 132.93 (d), 134.54 (d), 135.54 (s), 168.59 (s). Selective decoupling of the ethylenic protons resulted in a dramatically greater intensity for the peak at 134.54, relative to the other protonated carbons.

The following maleimides were purified for use in this study:

***N*-(4-Fluorophenyl)maleimide [1-(4-Fluorophenyl)-1*H*-pyrrole-2,5-dione] (7).** Recrystallization from cyclohexane yielded long, pale-green needles, mp 155–156 °C (lit.[19] mp 155 °C).

Recrystallization from cyclohexane yielded long, pale-green needles, mp 155–156 °C (lit.[19] mp 155 °C).

$^{13}C$ NMR ($CDCl_3$, letters denote actual multiplicities, *J*'s are $^{13}C$–$^{19}F$ coupling constants in hertz) $\delta$ 116.13 (d, $J = 22.6$), 127.22 (d, $J = 3.1$), 127.91 (d, $J = 8.54$), 134.22 (s), 161.81 (d, $J = 247.8$), 169.36 (s). Selective irradiation of the ethylenic protons resulted in enhancement of the intensity of the resonance at 134.22, relative to the other protonated carbons.

***N*-(4-Chlorophenyl)maleimide [1-(4-Chlorophenyl)-1*H*-pyrrole-2,5-dione] (8).** Recrystallization from cyclohexane gave light-yellow needles, mp 113–115 °C (lit.[25] mp 114 °C).

$^{13}C$ NMR ($CDCl_3$) $\delta$ 127.08 (d), 129.18 (d), 129.88 (s), 133.39 (s), 134.17 (d), 169.05 (s). Irradiation of the ethylenic protons resulted in enhancement of the intensity of the peak at 134.17, *relative to the other carbon resonances.*

***N*-(4-Bromophenyl)maleimide [1-(4-Bromophenyl)-1*H*-pyrrole-2,5-dione] (9).** Recrystallization of this compound from cyclohexane yielded bright-yellow needles, mp 123–124 °C (lit.[26] mp 118–120 °C).

$^{13}C$ NMR ($CDCl_3$) $\delta$ 121.43 (s), 127.33 (d), 130.32 (s), 132.18 (d), 134.20 (d), 168.97 (s). Selective irradiation of the ethylenic protons resulted in enhancement of the $^{13}C$ resonance at 134.20, relative to the other carbon resonances.

***N*-(4-Nitrophenyl)maleimide [1-(4-Nitrophenyl)-1*H*-pyrrole-2,5-dione] (10).** Recrystallization of this compound from ethanol–cyclohexane (1:3) gave colorless crystals, mp 167.5–169.5 °C (lit.[25] mp 163–165 °C).

$^{13}C$ NMR ($CDCl_3$) $\delta$ 124.48 (d), 125.45 (d), 134.61 (d), 137.10 (s), 146.21 (s), 168.49 (s).

***N*-(4-Carbethoxyphenyl)maleimide [4-(2,5-Dihydro-2,5-dioxo-1*H*-pyrrol-1-yl)benzoic Acid, Ethyl Ester] (11).** This compound was kindly provided by David P. Vanderbilt.[17] Recrystallization from cyclohexane yielded pale-yellow needles, mp 112–113 °C (lit.[27] mp 113 °C).

$^{13}C$ NMR ($CDCl_3$) $\delta$ 14.30 (q), 61.16 (t), 125.18 (d), 129.47 (s), 130.35 (d), 134.37 (d), 135.37 (s), 165.71 (s), 168.95 (s). Selective irradiation of the ethylenic protons resulted in enhanced intensity for the $^{13}C$ peak at 134.37, relative to the other carbon resonances.

***N*-(4-Methylphenyl)maleimide [1-(4-Methylphenyl)-1*H*-pyrrole-2,5-dione] (12).** Recrystallization from cyclohexane yielded yellow needles, mp 151.5–152 °C (lit.[28] mp 148.5–150 °C).

$^{13}C$ NMR ($CDCl_3$) $\delta$ 21.10 (q), 126.01 (d), 128.57 (s), 129.74 (d), 134.13 (d), 137.98 (s), 169.63 (s). Selective irradiation of the ethylenic protons resulted in enhancement of the $^{13}C$ signal at 134.13, relative to the other carbon resonances.

***N*-(4-(Acetyloxy)phenyl)maleimide [1-(4-(Acetyloxy)-phenyl)-1*H*-pyrrole-2,5-dione] (13).** Recrystallization from cyclohexane yielded pale-yellow needles, mp 160–161 °C (lit.[29] mp 156 °C).

$^{13}C$ NMR ($CDCl_3$) $\delta$ 21.03 (q), 122.23 (d), 126.91 (d), 128.76 (s), 137.17 (d), 149.79 (s), 169.00 (s), 169.29 (s). Selective irradiation of the ethylenic protons resulted in enhanced intensity for the $^{13}C$ peak at 134.17, *relative to the other carbon resonances.*

***N*-(4-Methoxyphenyl)maleimide [1-(4-Methoxyphenyl)-1*H*-pyrrole-2,5-dione] (14).** Recrystallization from cyclohexane yielded very bright-yellow needles, mp 148–151 °C (lit.[25] mp 146 °C).

$^{13}C$ NMR ($CDCl_3$) $\delta$ 55.44 (q), 114.44 (d), 123.84 (s), 127.57 (d), 134.08 (d), 159.13 (s), 169.78 (s). Selective irradiation of the ethylenic protons resulted in enhancement of the intensity of the $^{13}C$ peak at 134.08, relative to the other carbons.

The $^1H$ NMR, IR, and LRMS data for these compounds are included in supplementary material.

**Copolymer Synthesis and Characterization. Copolymer Synthesis.** All copolymers were synthesized in roughly the same manner. Azobis(isobutyronitrile) (AIBN, Aldrich) was used as the initiator in all cases, except where noted otherwise. The initiator was purified by recrystallization from methanol.

Purification of 2-chloroethyl vinyl ether (CEVE) (Aldrich), ethyl vinyl ether (EVE) (Aldrich), and *n*-butyl vinyl ether (BVE) (Aldrich) was carried out by stirring over calcium hydride for at least 24 h, followed by distillation. Methyl vinyl ether (MVE)

(Matheson) was condensed from the cylinder into a 250-mL round-bottomed flask which was cooled with an ice–water–salt mixture. The flask was then connected to a dry polymerization tube and allowed to warm to room temperature while the tube was cooled in a dry ice–2-propanol bath.

Maleimides were recrystallized from cyclohexane before use. Dichloromethane was distilled from phosphorus pentoxide. Benzene was stirred over 18 M $H_2SO_4$ for 24 h and then was decanted and distilled.

Typically, solutions of the desired concentrations were made by weighing appropriate amounts of the initiator, maleimide, and vinyl ether into a volumetric flask and diluting to the mark with solvent. The desired volume of this solution was then introduced into a clean polymerization tube with a pipette. The tube was connected to a high-vacuum line and degassed by at least 5 freeze–pump–thaw cycles and then sealed off at $<10^{-5}$ mmHg. Tubes thus prepared were placed in a bath (water, oil, or 2-propanol–dry ice) of the appropriate temperature for the desired amount of time. At the end of this time, the tube was removed from the bath, cooled to −78 °C in a dry ice–2-propanol bath, and opened. The solution was then slowly added dropwise to a large excess of rapidly stirred precipitation solvent (methanol was used unless otherwise noted). In some cases, it was necessary to redissolve the copolymer in acetone and precipitate it again in order to obtain a pure-white product.

It was noted that monomer solutions containing initiator decolorized on standing in bright light. Precipitation of these solutions, as described above, yielded pure-white copolymers. Thus, polymerizations described from now on as being carried out at "room temperature" took place in the presence of oxygen without careful temperature control.

In a copolymerization carried out at −78 °C, a Hanovia utility quartz ultraviolet lamp was used as a light source. The degassed monomer solution was placed in a dry ice–2-propanol bath, and the light was shone through a recrystallizing dish containing about 3 in. of water, which was placed on top of the Dewar flask containing the cold bath and tube. The water served as insulation, so that rapid heating of the bath by the hot lamp was avoided. Independent experiments showed that no copolymerization took place in the absence of initiator under these conditions. A UV scan showed that AIBN has an absorption maximum near 345 nm which is well above the Pyrex glass cutoff of about 280 nm.[15]

All 4-substituted phenyl maleimides copolymerized with 2-chloroethyl vinyl ether except for *N*-(4-nitrophenyl)maleimide, which yielded no copolymer after being heated in the presence of initiator and CEVE for 42 h in a 60.0 °C bath. The unreacted maleimide could be recovered unchanged (as judged by IR spectroscopy). A Sargent Thermonitor (Model S-W) constant-temperature bath was used to control the temperature of the water bath to 60.0 ± 0.1 °C. The homopolymer of *N*-phenylmaleimide was prepared in exactly the same way as the copolymers (i.e., AIBN, $CH_2Cl_2$, 60.0 °C).

The copolymerization conditions, yields, and combustion analysis data for all copolymerizations, except for those performed in kinetic studies, are given as supplementary material.

**2-Chloroethyl Vinyl Ether Homopolymer.** The 2-chloroethyl vinyl ether (CEVE) homopolymer was obtained from a sample of distilled CEVE which had been stored over unactivated molecular sieves (Linde) for several months. The NMR data for this material were consistent with those reported[30] for the CEVE homopolymer prepared in methylene chloride using boron trifluoride etherate catalyst. The $^{13}C$ NMR data are shown. $^1H$ NMR and IR data are included in supplementary material.

$^{13}C$ NMR ($CDCl_3$, internal reference $CDCl_3$ = 77.0[24]) $\delta$ 39.3 (t, br), 40.5 (t, br), 43.64 (t), 68.57 (t), 73.49 (d).

**Copolymerization Kinetics.** The initial rate of copolymerization for the system (NPM, CEVE, $CH_2Cl_2$, AIBN, 60.0 °C) was measured as a function of the mole fraction of maleimide in the initial comonomer feed ($\chi_M$) at constant total monomer concentration ($[M_1] + [M_2] = M_T$). A gravimetric technique was used to follow the conversion of monomers to polymer; i.e., the mass of copolymer formed was monitored as a function of time.

Solutions of the desired concentrations were made by weighing the appropriate amounts of monomers and initiators into clean 100-mL volumetric flasks and diluting to the mark with freshly distilled (from $P_4O_{10}$) dichloromethane. These solutions were transferred in 10-mL portions via pipette into clean, dry polymerization tubes. The tubes were connected to a high-vacuum line, degassed via 5 freeze–pump–thaw cycles, and sealed at $\leq 10^{-5}$ mmHg. The tubes were then immersed in a 60.0 ± 0.1 °C water bath. After the desired amount of time had elapsed, a tube was removed from the bath and immediately plunged into a dry ice–2-propanol bath. The time interval between immersions in the 60.0 and −78 °C baths was taken as the polymerization time and was measured with a stopwatch. The polymerization times were such that the conversion to polymer was low (≤10% of the initial weight of monomers present), so that the ratio of monomer concentrations was approximately constant. The cold tube was opened as quickly as possible, and the contents were quickly added to 100 mL of methanol in one portion. The tube was carefully rinsed with several portions of dichloromethane which were added to the methanol. The polymer was then filtered into clean, previously weighed fine-porosity, fritted-glass filters. The filter and polymer were then dried to constant weight, and the weight of the polymer was calculated by the difference.

**Copolymer Characterization.** **$^{13}C$ NMR.** Carbon-13 NMR analysis of the copolymers proved to be vastly superior to proton ($^1H$) NMR because of greater spectral simplicity resulting from the lack of coupling and the greater spectral width. $^1H$ NMR spectra of the maleimide–vinyl ether copolymers prepared in this study generally appear as a series of overlapping broad humps. All spectra were obtained in solution, and the solvent used was either $Me_2SO$-$d_6$ or tetrachloroethane (TCE). When TCE was used as the solvent, 10–15 drops of benzene-$d_6$ or toluene-$d_8$ were added for internal deuterium lock. Hexamethyldisiloxane (Merck & Co., 1–2 drops) was used as a reference (2.03 ppm from $Me_4Si$[31]) when TCE was used as the solvent. The middle peak of the solvent heptet (39.50 ppm from $Me_4Si$[24]) was used as the reference peak when $Me_2SO$-$d_6$ was the solvent. All spectra were run at high temperature. Acceptable line widths could be obtained at 100–110 °C for copolymers dissolved in $Me_2SO$-$d_6$ and at 70–80 °C for those dissolved in TCE.

Typical instrument parameters for obtaining polymer spectra were as follows: number of accumulations = 20 000–35 000; observation frequency = 47.0 kHz (TCE solvent), 47.3 kHz ($Me_2SO$-$d_6$ solvent); pulse width = 12–18 $\mu$s (60–90°); pulse delay = 180–360 ms; acquisition time = 0.819 s; spectral width = 5000 Hz; exponential line broadening = 0.97 Hz. Each spectrum required 8–10 h of accumulation. Acceptable signal-to-noise ratio was not attained when the $^{13}C$ NMR spectrum of NPM homopolymer was run, until 250 000 scans had accumulated.

**Copolymer $T_1$ Determination.** The spin–lattice relaxation times ($T_1$) were determined for the carbons in an NPM–CEVE copolymer prepared in bulk. The method used for this determination was the saturation recovery method developed by McDonald and Leigh.[32] The relaxation times were calculated by plotting ln $[S_\infty - S(\tau)]$ vs. $\tau$,[32] where $S_\infty$ and $S(\tau)$ were the signal areas corresponding to pulse intervals of infinity and $\tau$, respectively. The slope of these plots represents the relaxation time ($T_1$) for each carbon.

By using a 10-mm tube and a high copolymer concentration, a fairly good signal-to-noise ratio was obtained after 2 000 scans had been accumulated. Thus, up to 10 spectra could be obtained (each resulting from a different $\tau$) in a reasonable amount of time (12–24 h). The peaks were integrated electronically. Since the peaks were generally broad, and the signal-to-noise ratio was low (especially when short $\tau$'s were used), the integration was subject to error. Several experiments were run using various combinations of pulse intervals and $\tau_\infty$. This was necessary because of the large range of $T_1$ values encountered for different carbon types in the copolymer (22–3 000 ms); i.e., the $\tau$'s needed to measure the short $T_1$'s were not suitable for the measurement of long $T_1$'s and vice versa.

**Determination of Copolymer Nuclear Overhauser Enhancements (NOE).** Copolymer $^{13}C$ NOE's were determined by using the gated decoupling technique.[33] A spectrum was obtained by using complete decoupling. The pulse delay used to obtain this spectrum was 15 s (>5 times the longest $T_1$). The areas for all of the carbon resonances were measured. Another spectrum was run under exactly the same conditions, except the decoupler was gated on during data acquisition and off during the pulse delay. Thus, a proton decoupled spectrum was obtained, but without the NOE. The ratio of the areas obtained by using complete decoupling, and those obtained using gated decoupling, gives the NOE ratio. The quantity NOE-1 gives the amount of signal enhancement and is known as the nuclear Overhauser enhancement factor (NOEF).[34] Repeating the gated decoupled spectrum after adding some chromium tris(acetylacetonate) [(Cr(acac)$_3$][33] paramagnetic relaxation reagent had no effect on the integrated areas relative to those obtained without Cr(acac)$_3$.

**Copolymer Molecular Weight Determinations.** Several copolymers were characterized by gel permeation chromatography (GPC) or vapor pressure osmometry (VPO). A low conversion NPM–CEVE copolymer ($\chi_M = 0.2$, $M_T = 0.5$, AIBN, 60 °C) was analyzed on a Waters Model 6000-A GPC, which was equipped with a Model 440 absorbance detector. A Waters $10^4$ $\mu$Styragel column was used for the analysis. The peak maximum corresponded to a molecular weight of about 6300, based on polystyrene calibration curves. This molecular weight corresponds to a degree of polymerization (DP) of 22–23 (based on 1:1 repeat unit).

Vapor pressure osmometry analysis of a high conversion NPM–CEVE copolymer in acetone, using a benzil calibration standard, gave a number-average molecular weight ($\bar{M}_n$) of 13 250, which corresponds to a DP of 47–48.

**Copolymer Epimerization.** Maleimide–vinyl ether copolymers were epimerized by using several different bases and various reaction conditions. These conditions are detailed below.

**Copolymer Epimerization with 2,2,6,6-Tetramethylpiperidine (TMP) in Me$_2$SO.** The copolymer to be epimerized was dissolved in Me$_2$SO-$d_6$ (~0.25 g of copolymer/0.3 mL of Me$_2$SO-$d_6$), and several drops of TMP were added to the solution. Within 10–15 min, the solution turned from colorless to a deep cobalt blue color. The solution was filtered through a plug of glass wool into a clean, 5-mm NMR tube, which was capped and placed in a 60.0 °C water bath. The progress of the epimerization could thus be monitored by periodically obtaining a $^{13}$C NMR spectrum of the sample.

**Copolymer Epimerization with Lithium Diisopropylamide (LDA) in THF.** A three-necked, 200-mL round-bottomed flask equipped with a magnetic stirring bar, addition funnel, and nitrogen inlet was dried for several hours in a 140 °C oven and then allowed to cool in a dry nitrogen stream. One gram of the copolymer was dissolved in 20 mL of THF (freshly distilled from lithium aluminum hydride), and the resulting solution was placed in the addition funnel. About 1.0 g solid LDA (Alfa) was added to 75 mL of distilled THF which had been added to the reaction flask. The transfer of the LDA was performed under a blanket of dry nitrogen. The reaction flask was cooled to −75 °C with a dry ice–2-propanol bath. The LDA solution was magnetically stirred under positive nitrogen pressure, as the copolymer solution was slowly added over 10 min. The solution turned from colorless to deep red, and finally to black opaque, as the copolymer solution was added. This solution was stirred at −75 °C for 1 h, after which the solution was deep green. Approximately 30 mL of saturated aqueous ammonium chloride was quickly added while the solution temperature was still −75 °C. The ammonium chloride solution froze on contact with the cold THF. The dry ice was allowed to evaporate, so the solution slowly warmed to room temperature with continued stirring. The organic layer of the resulting two-phase system was now a deep cobalt blue color. The organic layer was separated and added dropwise to rapidly stirred methanol. The resulting light-blue precipitate was filtered and dried overnight at reduced pressure (50 °C) to yield 0.9 g of light-blue powder. About half of this powder was treated with 20 mL of hot (80 °C) acetic anhydride for 3 h. The deep-green copolymer solution that resulted was allowed to cool, and 75 mL of water was added. The resulting precipitate was filtered and dried in vacuo. The resulting light-green powder was dissolved in acetone and precipitated into methanol. Three additional precipitations from acetone into methanol failed to rid the product of all of its green color.

IR analysis of the original blue copolymer showed a broad peak at 3150 cm$^{-1}$, which may be due to an amide N–H stretch resulting from partial hydrolysis of the succinimide units of the copolymer. This band disappeared on treatment of the copolymer with hot acetic anhydride. Otherwise, the IR spectrum of the epimerized copolymer was unchanged from that of the copolymer before epimerization.

**Copolymer Epimerization with Potassium *tert*-Butoxide in Me$_2$SO.** Potassium *tert*-butoxide was synthesized by using high-vacuum techniques. About 5 mL of *tert*-butyl alcohol was distilled from calcium oxide and sealed into a break-seal. About 20 mL of freshly distilled (from KOH) Me$_2$SO was used to dissolve 3.5 g of copolymer, and the resulting solution was sealed into a clean break-seal. A solution of 1 g of ammonium chloride in 10 mL of distilled Me$_2$SO was sealed into a third break-seal. The three break-seals were attached to a 200-mL round-bottomed flask that could be attached to a vacuum line by means of a 14/20 ground-glass joint. The flask was also equipped with a side arm that had several constrictions through which potassium metal could be distilled. A small test tube with a ground-glass joint containing a pea-sized piece of potassium metal under hexane was connected to the side arm of the inverted apparatus. The whole apparatus was again inverted, quickly connected to the vacuum line, and evacuated. The potassium was gently heated with a yellow flame, causing it to melt and flow down the side arm. The reaction flask was cooled in ice water. Continued heating of the potassium metal caused it to distill onto the inside wall of the cool flask, forming a bluish-silver mirror. The side arm was sealed off, and the *tert*-butyl alcohol was introduced by breaking the corresponding break-seal. The metal was quickly consumed. Hydrogen gas was evolved, and a clear, colorless solution resulted. The break-seal containing the copolymer solution was then broken, allowing the solution to flow into the potassium *tert*-butoxide solution. Within 2 min, the combined solutions had gone from nearly colorless to deep green to a deep cobalt blue color. The blue solution was stirred at room temperature for 43 h, and the break-seal containing the ammonium chloride solution was broken. No color change was noted when the ammonium chloride solution was added. The bulk of the solvent was removed on the vacuum line with heat. The apparatus was removed from the vacuum line, chloroform was added to the bright-blue residue, and the chloroform solution was extracted with water. The organic layer was dried overnight over anhydrous MgSO$_4$. The MgSO$_4$ was separated from the solution by filtration. The blue chloroform solution was slowly added dropwise to rapidly stirred hexane to yield a blue precipitate. This precipitate was filtered and dried overnight in a 50 °C vacuum oven to yield 3.0 g of light-blue powder. The IR spectrum of the epimerized copolymer was nearly identical with that of the copolymer before epimerization, except for a small decrease in the relative intensity of the peak at 1110 cm$^{-1}$.

**Complexation Studies.** Ultraviolet (UV) spectroscopy was used to study the complexation behavior of maleimides and CEVE. Dichloromethane (CH$_2$Cl$_2$) was used as the solvent in all cases. Invariably, the solvent was distilled from P$_4$O$_{10}$ immediately prior to its use. CEVE was distilled from calcium hydride immediately before use. The maleimides investigated were *N*-(4-methoxyphenyl)-, *N*-(4-chlorophenyl)-, *N*-phenyl-, *N*-(4-(trifluoromethyl)phenyl)-, *N*-(4-cyanophenyl)-, and *N*-cyclohexylmaleimides.

Solutions of CEVE in CH$_2$Cl$_2$ have absorptions with $\Delta_{max}$ 275, 262, and 254 nm. Dichloromethane solutions of *N*-arylmaleimides have absorptions with $\Delta_{max}$ in the range 300–320 nm and $\Delta_{max}$ 255–275 nm, depending on the maleimide. In contrast to solutions of *N*-arylmaleimides, *N*-cyclohexylmaleimide solutions did not have an absorption at 255 nm. Addition of equal amounts of CEVE to a maleimide solution in the sample beam of the UV spectrometer and a solvent blank in the reference beam results in a slight intensification of the absorbance in the 255–300-nm region. This increase in absorbance was attributed to the formation of a DA and was therefore investigated further.

The experiments involved the monitoring of the absorbance of maleimide–CEVE solutions of constant maleimide concentration and varying CEVE concentration. The [CEVE] was always much greater than the [maleimide]. In a typical procedure, the spectrum of the pure maleimide in CH$_2$Cl$_2$ was measured against a reference of pure CH$_2$Cl$_2$ by using a pair of 2-mm quartz cuvettes. Next, the spectrum of the solution of the maleimide and vinyl ether was measured against a reference containing the vinyl ether at the same concentration. The first spectrum was subtracted from the second to afford the spectrum of the DA. Absorbances were read directly from the digital display at 5-nm intervals.

Solution concentrations were carefully controlled so that [maleimide] was the same in all runs and [CEVE] was exactly the same in both reference and sample cells. Stock solutions of maleimide and CEVE were made by weighing the desired amounts of monomers into clean, dry volumetric flasks and diluting to the

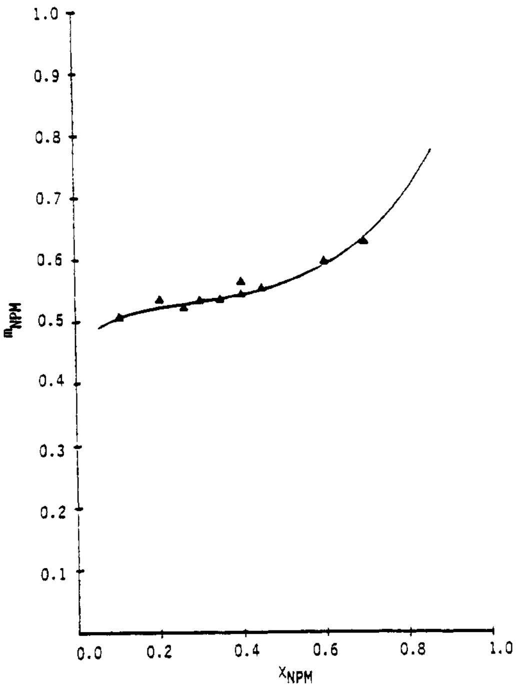


**Figure 1.** Copolymer composition diagram for the NPM-CEVE system ($m_{NPM}$ = mole fraction NPM in the copolymer, $\chi_{NPM}$ = initial mole fraction of NPM in the feed; constant $M_T$ = [NPM] + [CEVE] = 0.5, $CH_2Cl_2$, AIBN, 60 °C).

mark with solvent. Experimental solutions were then made by transferring the appropriate amounts of the stock solutions to a series of volumetric flasks with glass pipettes, followed by dilution to the mark. Convenient final concentrations for the maleimide solutions were approximately 0.01 M. CEVE concentrations varied in the range 0.3-2.5 M.

**Model Compounds.** The synthesis and stereochemical assignments of the model compounds discussed in this work have been described in a separate paper.[35]

## Results and Discussion

Various N-substituted maleimides were shown to copolymerize alternately with several vinyl ethers. Chlorine and nitrogen elemental analysis of *N*-phenylmaleimide (NPM)-2-chloroethyl vinyl ether (CEVE) copolymers prepared by using conventional free radical initiation (AIBN, $CH_2Cl_2$, 60.0 °C) indicated that the copolymers contained nearly equimolar amounts of comonomers regardless of the comonomer mole ratio in the original monomer feed (Figure 1). The NPM-CEVE copolymerization rate exhibited a maximum at a nearly 1:1 initial comonomer mole ratio, where the DA complex concentration is expected to be maximum (Figure 2). Rate profiles such as this are typical of comonomer pairs that polymerize in an alternate manner.[11] Reactivity ratios derived from the composition data by using the Kelen-Tudos[36] method were $r_1$ = 0.284 (NPM) and $r_2$ = 0.008 (CEVE). The Joshi-Joshi[37] method for determining reactivity ratios yielded values of $r_1$ = 0.286 and $r_2$ = 0.000. These data show that NPM and CEVE copolymerize in an alternate manner and that CEVE has little or no tendency to homopolymerize under these conditions. The NPM monomer, however, does homopolymerize under free radical initiation, albeit at a slower rate (Figure 2). The homopolymerization of NPM has been previously investigated by several authors.[38,39]

**$^{13}C$ NMR Structural Studies on N-Substituted Maleimide-Vinyl Ether Copolymers. Peak Assignments.** Figure 3 shows the $^{13}C$ NMR spectrum of a NPM-CEVE copolymer prepared by using light-induced decomposition of AIBN at low temperature (-78 °C) and a large excess of CEVE [initial mole fraction of NPM ($\chi_M$) = 0.1] in the feed. Copolymers prepared under these conditions possessed totally alternating sequence distributions (as judged by elemental analysis). The peak assignments shown were made by utilizing several techniques. General assignments can be made by comparison with the considerable amount of $^{13}C$ shift data available in the literature.[34] The three peaks appearing in the 173-178 ppm region may be confidently assigned to carbonyl carbons. The peaks appearing in the 126-132 ppm region are due to aromatic carbon resonances. The chemical shifts of the peaks appearing in the range 69-77 ppm are consistent with those of carbons that are α to an oxygen atom.

An off-resonance-decoupled spectrum of the copolymer was run, and the peaks appearing at 131.9, 174.4, 175.6, and 177.1 remained as singlets. This means that the carbons resonating at these positions have no directly

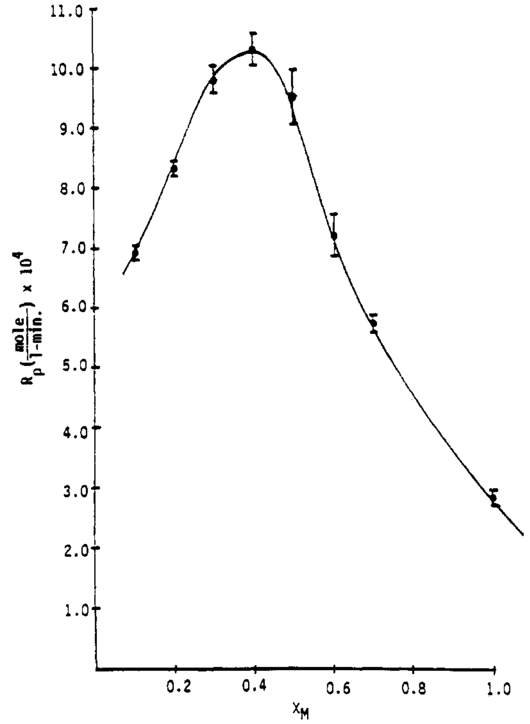


**Figure 2.** Initial copolymerization rate vs. $\chi_M$ for the system NPM, CEVE, AIBN, $CH_2Cl_2$, 60 °C. Error bars indicate two standard deviations of the slope of the [polymer] vs. time plots.

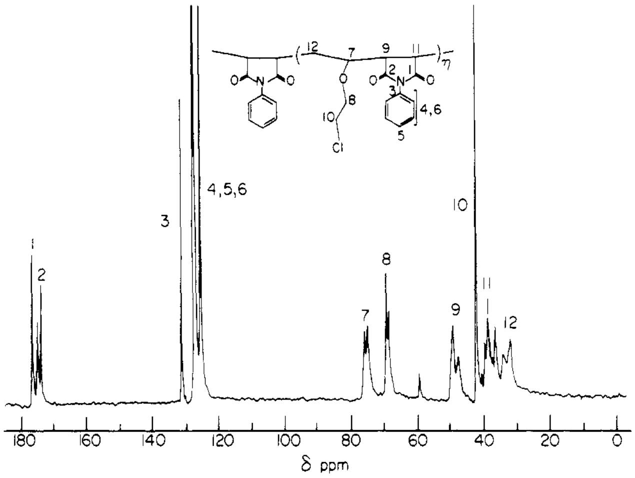


**Figure 3.** Noise-decoupled $^{13}C$ NMR spectrum of an NPM-CEVE copolymer; spectrum obtained in $Me_2SO\text{-}d_6$ at 110 °C.

**Table I**
**Carbon-13 Spin-Lattice Relaxation Times ($T_1$) and Nuclear Overhauser Enhancement Factors (NOEF) for an NPM-CEVE Copolymer[a]**

| carbon[b] | $\delta$[c] | $T_1$ range,[d] ms | av $T_1$, ms | NOE[e] | NOEF[f] |
|---|---|---|---|---|---|
| 1 | 177.1 | 1400–2200 | 2000 | 1.82 | 0.82 |
| 2 | 174.4–175.6 | 1400–1900 | 1400 | 1.81 | 0.81 |
| 3 | 131.9 | 2100–3000 | 2500 | 1.82 | 0.82 |
| 4,5[g] | 127.7–128.3 | 200–560 | 334 | 2.92 | 1.92 |
| 6 | 126.3 | 160–330 | 250 | 2.86 | 1.86 |
| 7 | 75.7–76.7 | 28–68 | 56 | 2.03 | 1.03 |
| 8 | 69.2–70.1 | 64–186 | 142 | 2.28 | 1.28 |
| 9 | 48.3–49.9 | 62–99 | 76 | 2.30 | 1.30 |
| 10 | 42.9 | 98–264 | 164 | 3.03 | 2.03 |
| 11 | 37.0–39.5 | under solvent ($Me_2SO$-$d_6$) resonance | | | |
| 12 | 32.4–34.7 | 22–35 | 29 | 2.59 | 1.59 |

[a] Prepared in bulk. [b] Numbered as in Figure 3 (low to high field). [c] Internal reference $Me_2SO$-$d_6$ = 39.5 ppm.[24] [d] Range of values determined in at least three separate experiments. [e] Theoretical maximum value is 2.988.[43] [f] Theoretical maximum value is 1.987.[34] [g] These peaks overlap.

bonded protons. This is consistent with the assignment of the carbonyl carbons. The resonance appearing at 131.9 was assigned to the quaternary aromatic carbon on the basis of this result. The other aromatic carbon peaks are split into doublets on off-resonance decoupling and thus are assigned to the ortho, meta, and para carbons of the phenyl ring. The small peak appearing as a shoulder at 127.7 ppm was assigned to the para carbon due to its small intensity. The ortho and meta carbons cannot be distinguished by this technique.

The peaks centered at 76 ppm split into doublets on off-resonance decoupling and were thus assigned to the methine carbon of the vinyl ether units in the copolymer. Similarly, the peaks centered at 69.7 ppm were split into triplets and were assigned to the methylene carbon of the side chain that is $\alpha$ to oxygen. The intense singlet appearing at 42.9 ppm was also split into a triplet in the off-resonance-decoupled spectrum. This peak was assigned to the methylene carbon $\alpha$ to chlorine in the vinyl ether units. The large intensity of this peak also supports this assignment. This carbon is located on a side chain three bonds from the nearest chiral center in the copolymer backbone and thus is not expected to be split or broadened significantly by the different magnetic environments produced by varying backbone stereochemistry.

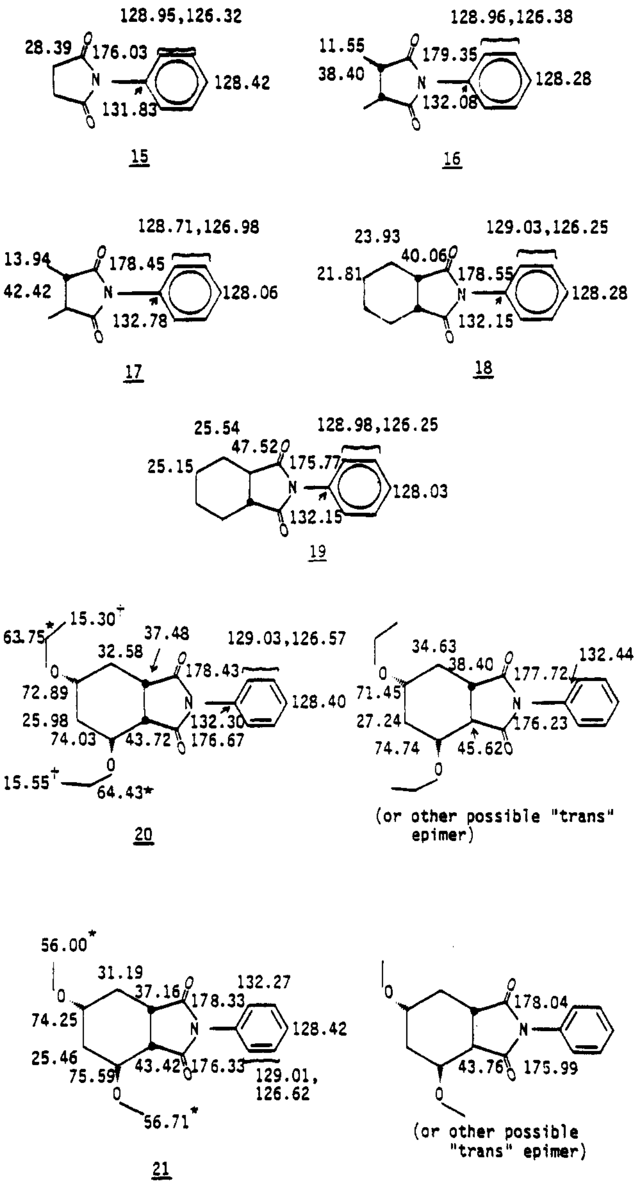
The remaining carbons (backbone methines of the succinimide units and the backbone methylene of the vinyl ether units) appear as fairly closely spaced broad resonances in the completely decoupled spectrum (31–50 ppm). The splitting induced by off-resonance decoupling causes these peaks to be even broader, and considerable overlap of peaks was observed. Careful examination of expansions of this region allowed tentative assignment of the highest field resonance (32–34 ppm) to the backbone methylene carbon of the vinyl ether units. This assignment was supported by the $^{13}C$ spin-lattice relaxation times ($T_1$) compiled in Table I. Polymer backbone $T_1$'s for methylene carbons are generally half the $T_1$ values of backbone methine carbons because of the greater efficiency of the dipolar relaxation mechanism resulting from two directly bonded protons (methylene) as opposed to a single directly bonded proton (methine).[40,41] As shown in Table I, the $T_1$ of the resonance appearing farthest upfield (32–34 ppm) was about 29 ms, and the $T_1$ for the resonance at 48–50 ppm was about 76 ms. Thus, the resonance at 32–34 ppm could more confidently be assigned to the backbone methylene of the vinyl ether units.

The $T_1$'s listed in Table I also support the assignments discussed above. Quaternary carbons generally have long $T_1$'s,[32,33] and the values determined for the resonances assigned to the carbonyl and quaternary aromatic carbons are much longer ($\sim$10 times) than the rest of the values determined. The $T_1$ values of the resonances assigned to the methine $\alpha$ to oxygen (56 ms) is about half of the $T_1$ determined for the side chain methylene $\alpha$ to oxygen (142 ms). This finding supports the assignment for the reasons discussed above.

The assignment of the intense resonance at 42.9 ppm to the side chain methylene carbon $\alpha$ to chlorine is supported by the NOEF values listed in Table I. The NOEF values for polymer carbons are often less than the theoretical maximum of $\sim$2, due to the fact that the effective correlation time (related to the tumbling rate or segmental reorientation rate) does not satisfy the extreme narrowing condition ($\omega_0\tau_c \ll 1$, where $\tau_c$ is the correlation time, and $\omega_0$ is the Larmor frequency).[40] This is true for all carbons listed in Table I except for the carbon resonating at 42.9 ppm (and the protonated aromatic carbons), which exhibit the full theoretical NOE. This is to be expected if the carbon is part of a relatively flexible side chain.[34,40]

The distinction between the two methine and the two carbonyl carbons of the succinimide units cannot be made by use of the off-resonance decoupling technique or by comparing $T_1$ or NOEF values. A good estimate of the relative chemical shifts of such similar carbon types can be made by exploiting the chemical shift parameters first determined by Grant and Paul,[42] and extended by Lindeman and Adams,[43] for various alkanes. Tonelli et al.[44-46] have utilized similar considerations to predict the $^{13}C$ spectra of many homo- and copolymers. In general, these authors have shown, by empirical comparison of the $^{13}C$ chemical shifts of a large number of compounds, that atoms other than protons $\alpha$ or $\beta$ to a carbon of interest cause a downfield shift ($\sim$9 ppm for carbon atoms) relative to a similar compound without the substitution. Atoms other than protons that are $\gamma$, and situated in a gauche relationship to the carbon of interest, on the other hand, cause an upfield shift, the magnitude of which depends on the atom and the probability that the $\gamma$ substituent is gauche to the carbon of interest. Examination of the copolymer structure (Figure 3) reveals that both carbonyls of the succinimide units have the same number of $\alpha$ and $\beta$ atoms, but carbonyl 2 has an extra $\gamma$ interaction (O atom of the vinyl ether) in comparison with carbonyl 1. Thus, the upfield carbonyl resonance was assigned to carbonyl 2. Similarly, methine carbons 9 and 11 both are $\alpha$ to the same number of atoms. Carbon 9 has an extra $\beta$ interaction compared to carbon 11, while carbon 11 has one more $\gamma$ interaction than carbon 9. Thus, the resonance overlapped by the solvent ($Me_2SO$-$d_6$) at $\sim$37–40 ppm was assigned to carbon 11, and the downfield methine ($\sim$48–50 ppm) was assigned to carbon 9.

The structures and $^{13}C$ chemical shifts for the model compounds synthesized in this work are shown in Figure 4. The copolymer structure and the chemical shifts based on the above assignments are shown in Figure 5, along with the $^{13}C$ chemical shifts of the CEVE and NPM homopolymers. While it may be argued that the model compounds do not have structures that are strictly analogous to the copolymer structure because some of them have a bicyclic structure, it is felt that they are useful for qualitative comparisons. The model compounds could be synthesized in stereospecific form and could be more easily characterized by proton NMR than the copolymers.



*,+ assignments could be reversed

**Figure 4.** Model compound $^{13}$C NMR chemical shifts ($CDCl_3$, ppm from $Me_4Si$).

It can be seen from Figures 4 and 5 that the chemical shifts of the model compounds are in qualitative agreement with the assignments of the copolymer resonances discussed above.

The differences in the chemical shifts for similar carbons in the homo- and copolymers (see Figure 5), coupled with the fact that the copolymers contain a nearly 1:1 mole ratio of the comonomers (see Figure 1), may be taken as additional evidence for the alternating nature of these copolymers.

**Interpretation of Copolymer $^{13}$C Spectra.** The copolymer whose $^{13}$C NMR spectrum is shown in Figure 3 contains a 1:1 ratio of comonomers and is believed to be totally alternating (vide supra). The spectrum exhibits fewer peaks than might be expected, based on the fact that there are three chiral centers per alternating repeat unit. Free radically initiated polymers are typically predominantly atactic, with a slight preference for syndiotactic placement.[47] Thus, as a first approximation, all possible relative stereochemical structures should be present to a greater or lesser extent. $^{13}$C NMR is very sensitive to differences in magnetic environment caused by differences in relative stereochemistry between chiral centers in polymers.[31,34,40] The sensitivity of $^{13}$C chemical shifts to different stereochemical environments usually decreases rapidly with distance. In other words, a carbon of interest is often most sensitive to differing relative stereochemistry between chiral centers situated one bond away, and less sensitive to relative stereochemistry between chiral centers two bonds distant, and so on. Sensitive, in this context, refers to the magnitude of the chemical shift difference caused by varying stereochemical placements. The possible relative stereochemical structures between adjacent chiral centers ("dyad" stereochemistry) in NPM–CEVE

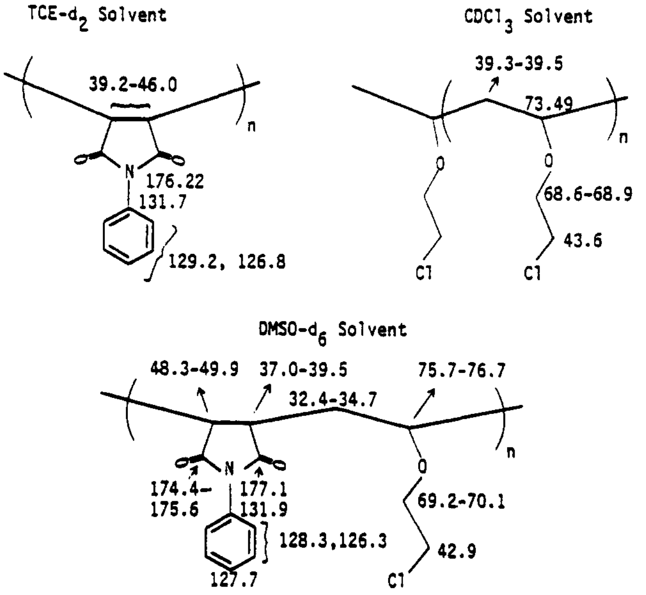


**Figure 5.** Homo- and copolymer $^{13}$C NMR chemical shifts (ppm from $Me_4Si$).

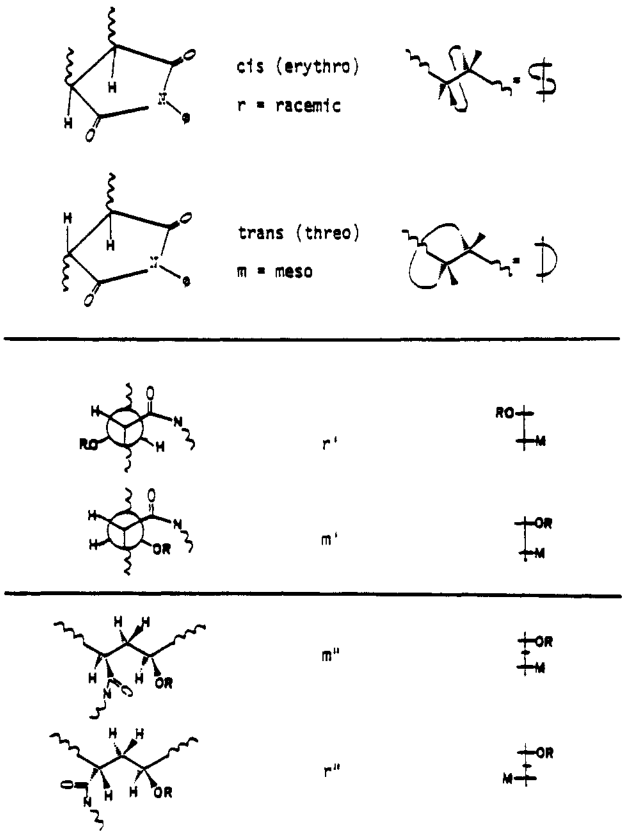


**Figure 6.** "Dyad" stereochemical possibilities for NPM–CEVE alternating copolymers (i.e., relative stereochemistry between two adjacent chiral centers).

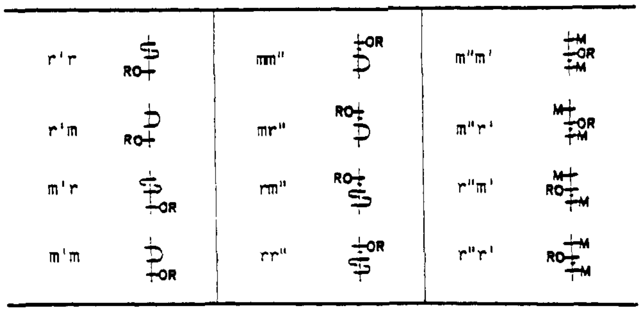


**Figure 7.** "Triad" stereochemical possibilities for alternating sequences in NPM–CEVE copolymers.

alternating copolymers is shown in Figure 6. Figure 7 illustrates the various stereochemical possibilities for three adjacent chiral centers ("triads") for alternating sequences. As can be seen in Figure 3, many of the $^{13}C$ resonances do not appear as singlets but are split. Since this copolymer is not expected to exhibit complications due to varying sequence distribution, these splittings are presumed to reflect dyad stereochemical sensitivity.

Consideration of the carbonyl region shows that if carbonyl 1 is sensitive to stereochemistry two bonds removed, it would be expected to appear as two peaks [m or r (Figure 7)]. If this carbon is sensitive to stereochemistry three bonds distant, it would appear as eight peaks (r′mm″, m′mm″, r′mr″, r′rm″, m′rm″, r′rr″, and m′rr″). If carbonyl 2 is sensitive to stereochemical differences two bonds removed, four peaks are expected [r′r, r′m, m′r, and m′m (Figure 7)], since this carbon is situated two bonds from two chiral centers and one bond from another. The experimental observation is three peaks in the carbonyl region with approximate area ratios of 2:1:1 (measured by electronic integration and by cutting and weighing). This observation can only be explained if the stereochemistry at the succinimide units is either exclusively cis (r) or trans (m), and both carbonyls can "see" at most relative stereochemistry two bonds distant. If this is the case, carbonyl 1 should appear as a singlet, and carbonyl 2 should appear as two peaks (split only by the relative stereochemistry between carbons 7 and 9, r′ or m′).

The fact that the area ratio of the two peaks comprising the resonance ascribed to carbonyl 2 is about 1:1 (the downfield peak is slightly broader) may indicate that the relative stereochemistry between carbons 7 and 9 is random (~50% r′ and ~50% m′). This contention is supported by the fact that the resonance assigned to carbon 7 also appears as two peaks with approximately 1:1 area ratio. Thus, it appears that carbon 7 is sensitive only to relative stereochemistry resulting from the chiral center that is one bond away (carbon 9).

Carbon 8 also appears as two peaks, but the area ratio is clearly not 1:1. Apparently, carbon 8 exhibits different stereochemical sensitivity than carbon 7. This has been found to be true in the case of various vinyl ether homopolymers. The methine carbon of poly(ethyl vinyl ether) appears as a singlet, while the methylene in the side chain exhibits triad configurational sensitivity. The backbone methylene has dyad sensitivity.[48] In the $^{13}C$ NMR spectrum of poly(methyl vinyl ether), the methyl carbons show splitting which has been ascribed to pentad configurational sensitivity, while the methine appears as a singlet.[48]

In view of the fact that the methoxy carbon in poly(methyl vinyl ether) is very sensitive to various configurational sequences, an NPM–methyl vinyl ether (MVE) copolymer was synthesized. The methoxy carbon is clearly split into three peaks, while the methine of the vinyl ether unit appears as a singlet. This observation may be taken as evidence that the side chain carbons of the vinyl ether units in NPM–vinyl ether copolymers are more sensitive to configurational sequences than the methine carbons.

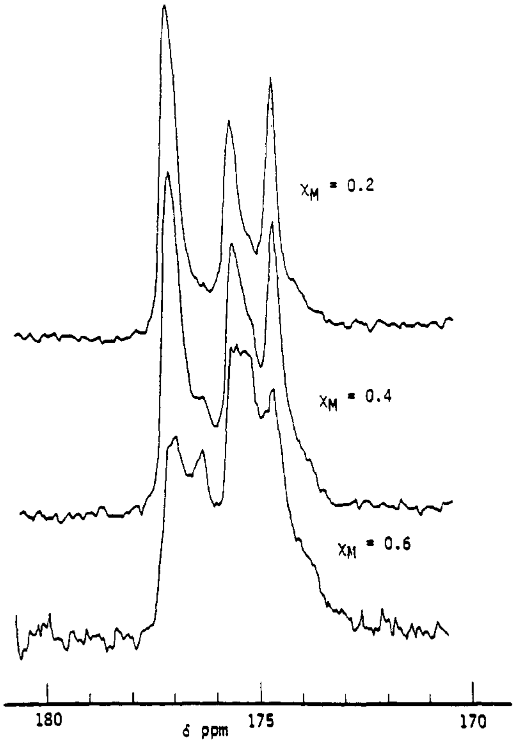


**Figure 8.** Effect of the mole fraction of NPM in the initial comonomer feed ($\chi_M$) on the appearance of copolymer $^{13}C$ NMR carbonyl peaks.

Carbon 9 appears as two overlapping peaks having an approximate area ratio of 2:1. The corresponding peak in the $^{13}C$ NMR spectrum of the NPM–CEVE copolymer is a complex resonance consisting of at least eight overlapping peaks. Thus, this carbon is thought to be sensitive to longer configurational sequences than "dyads".

Carbon 11 also exhibits configurational splitting. This resonance was overlapped by the solvent peaks when the spectrum was run in $Me_2SO\text{-}d_6$. This problem could be circumvented by running the $^{13}C$ NMR spectrum in tetrachloroethane. The resonance then appears as two peaks with approximate area ratio of 1:1. It is possible that this splitting reflects the relative stereochemistry between carbons 11 and 7 (m″ or r″).

It is reasonable to assume that the splitting observed for the backbone methylene carbon 12 reflects the relative stereochemistry between carbons 11 and 7. This resonance consists of two overlapping broad peaks. The approximate area ratio of these two peaks is 1:1 (the downfield peak is broader). Although the accuracy of the area determination for overlapping peaks may be questioned (cut and weigh, planimetry, and electronic integration), the corresponding peaks in the $^{13}C$ NMR spectrum of the NPM–MVE copolymer are not as broad, and they exhibit base-line resolution. The area ratio for these peaks in the NPM–MVE copolymer is also 1:1, although the downfield peak is somewhat broader than the upfield peak. This observation is interpreted as indicating that the relative stereochemistry between chiral centers at carbons 7 and 11 is random. In other words, the probability for an m″ placement ($P$(m″)) is 0.5.

In summary, on the basis of $^{13}C$ NMR analysis, the stereochemistry at the succinimide units in the copolymers discussed is either all cis ($P$(r) = 1.0, $P$(m) = 0, or all trans ($P$(m) = 1.0, $P$(r) = 0), while the relative stereochemistry between chiral centers 7 and 9, and 7 and 11, appears to be random ($P(\mathrm{m}') \approx P(\mathrm{m}'') \approx 0.5$).

**Effect of Composition and Stereochemistry on Copolymer $^{13}$C NMR Spectra.** The appearance of copolymer $^{13}$C spectra depends markedly on the conditions used to synthesize the copolymers. Figure 8 shows expansions of the carbonyl region of $^{13}$C spectra of copolymers obtained with various initial comonomer mole fractions ($\chi_M$). Other conditions used to synthesize the copolymers whose spectra are shown in Figure 8 were exactly the same [temperature (60 °C), AIBN, $CH_2Cl_2$, $M_T = 0.5$]. Several changes are obvious in the spectra as the initial mole fraction of NPM is varied. First, the intensity of the peak at about 176.4 ppm increases at the expense of the peak at 177.1 ppm as the fraction of NPM in the initial feed is increased. Second, the upfield peaks seem to broaden and increase in intensity relative to the downfield peaks as $\chi_M$ increases.

As shown in Figure 1, the mole fraction of maleimide incorporated into the copolymer also increases somewhat as $\chi_M$ increases. Thus, one possible explanation for the observed changes in the $^{13}$C spectra is that the sequence distribution changes with $\chi_M$ (i.e., carbonyl carbons in sequence of two or three consecutive succinimide units may exhibit different chemical shifts than the carbonyls of succinimide units in alternating sequences). A second possibility is that the stereochemistry at the succinimide units affects the carbonyl $^{13}$C chemical shifts and it varies with the initial mole fraction of NPM present in the feed.

The changes shown in Figure 8 seem to be more dramatic than might be expected, based on the relatively small changes in copolymer composition in this range of $\chi_M$ (see Figure 1), if they are due to compositional sequence variations. Therefore, it was thought that the observed variations in the $^{13}$C NMR spectra were at least in part due to the differences in copolymer stereochemistry. This postulate was verified by epimerizing various NPM–CEVE copolymers by using different bases and epimerization conditions. These epimerizations presumably proceed via generation of the enolate of the succinimide by basic abstraction of the acidic proton $\alpha$ to the carbonyl. Protonation of the planar enolate should lead to a scrambling of the stereochemistry at the succinimide units of the copolymer.[49] Figure 9 shows the expanded carbonyl regions of NPM–CEVE copolymers at various stages of epimerization. It is obvious from these studies that the changes in the relative intensities of the peaks at 176.4 and 177.1 ppm, and the broadening of the carbonyl peaks farther upfield, are due to changes in the stereochemistry at the succinimide units in the copolymers.

Enolate generation with lithium diisopropylamide (LDA) in THF at low temperature is generally irreversible.[49] Therefore, on quenching with a proton source ($NH_4Cl$ in this case), approximately equal amounts of the possible diastereomers are expected. The copolymer carbonyl peaks at 176.4 and 177.1 ppm have a nearly 1:1 intensity ratio after epimerization with LDA. This result is exactly what is expected for carbonyl 1 (see Figure 3) if this carbonyl is sensitive to stereochemistry two bonds distant. The relative stereochemistry between carbons 9 and 11 is either all cis or all trans before epimerization, and the cis:trans ratio is about 1:1 after epimerization. As discussed in the preceding section, if the copolymer stereochemistry is random, then carbonyl 2 is expected to appear as four peaks. Four separate peaks are not clearly resolved in the LDA epimerized copolymer carbonyl region, but the peaks assigned to this carbon have clearly broadened upon epimerization. This observation is consistent with the expected result.

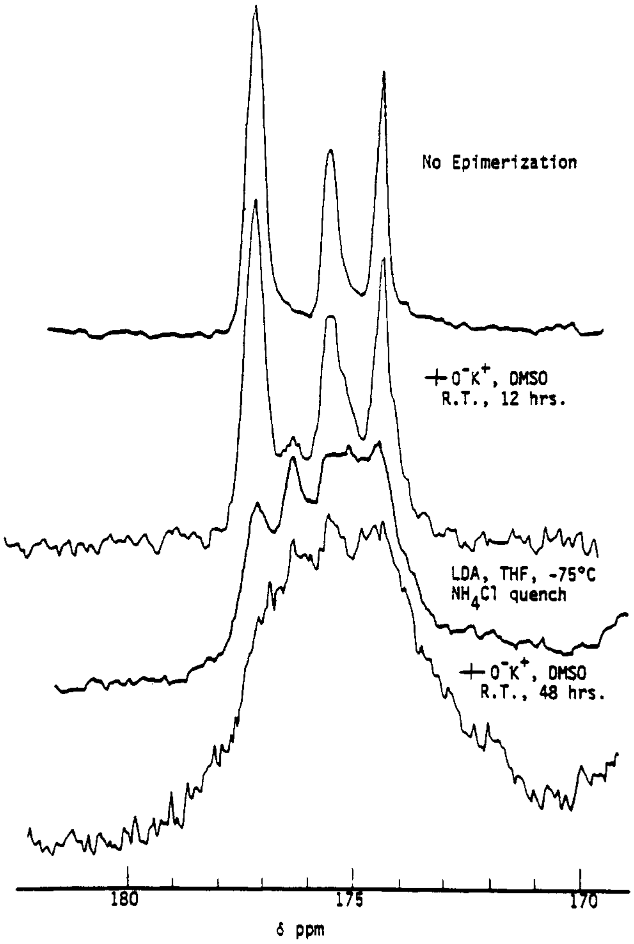


**Figure 9.** Effect of copolymer epimerization on the carbonyl region of the $^{13}$C NMR spectra of NPM–CEVE copolymers.

Copolymer composition data (Figure 1) indicate that the mole fraction of NPM in the copolymers increases slightly with the mole fraction of NPM in the feed, so there are undoubtedly some sequences of two, three, or more consecutive succinimide units in the copolymers. The carbonyls in these sequences could conceivably have different chemical shifts than carbonyls in succinimide units flanked by two ether units. The carbonyls of the NPM homopolymer appear as a fairly broad single peak with a maximum at ~176.2 ppm. The apparent increase in intensity of the upfield carbonyl resonances relative to the downfield peaks with increasing mole fraction NPM in the feed (see Figure 8) could be due to an increase in the percentage of succinimide homo repeat units in the copolymers. Supporting evidence for this postulate is given in Figure 10, which shows the carbonyl regions of the $^{13}$C NMR spectra of two NPM–CEVE copolymers prepared under the conditions: $M_t = 0.5$, $\chi_M = 0.7$, AIBN, 60 °C. Spectrum a was obtained on a high-conversion copolymer (<10%). Succinimide units comprise 67% and 62% of these two copolymers, respectively. The difference in the comonomer ratio in the copolymers is clearly reflected by an increased intensity of the upfield peaks, relative to those appearing downfield for the high-conversion copolymer.

Examination of the $^{13}$C chemical shifts determined for the model compounds (Figure 4) reveals that in all cases the carbonyl chemical shifts are greater for the compounds that possess a cis stereochemistry at the succinimide methines, as opposed to the corresponding compounds that have trans stereochemistry. Figure 9 shows that the peak at 176.4 ppm grows at the expense of the downfield peak at 177.1 ppm upon epimerization. These observations

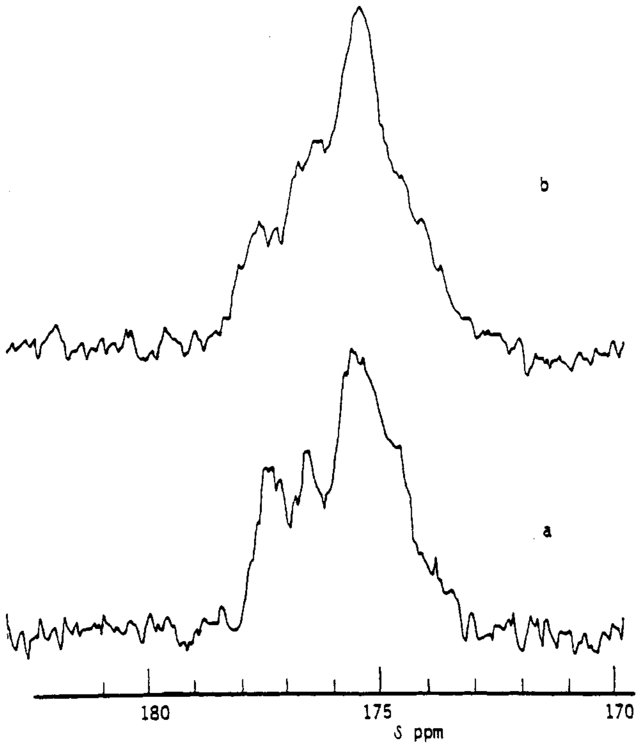


**Figure 10.** Expanded carbonyl regions of the $^{13}C$ NMR spectra of (a) low-conversion and (b) high-conversion NPM–CEVE copolymers ($\chi_M$ = 0.7, $M_T$ = 0.5).

suggest that the predominant relative stereochemistry at the succinimide units in NPM–CEVE copolymers is cis.

This contention is supported by the epimerization results shown in Figure 9. Long-term equilibrium epimerization of NPM–CEVE copolymers with the bases 2,2,6,6-tetramethylpiperidine (TMP) or potassium *tert*-butoxide in $Me_2SO$ resulted in the continued decrease of the intensity of the peak at 177.1, and continued increase of the peak at 176.4, until the downfield peak was the minor component. Trans stereochemistry at the succinimide units is expected to be favored thermodynamically, since epimerization of model compound **16**, under similar conditions (TMP, $Me_2SO$, 60 °C), resulted in a sixfold excess of the trans isomer. This could be due to a relief of steric strain in the cis compound on transformation to the trans. Similar relief of steric strain should also favor the trans form in the copolymer. As seen in Figure 9, the overlap of peaks in the $^{13}C$ NMR spectra of the equilibrium-epimerized copolymers is severe. It is felt, however, that the intensity at 177.1 ppm is definitely smaller than that at 176.4, and this fact is taken as solid evidence that NPM–CEVE copolymers possess predominantly cis stereochemistry at the succinimide units.

The possibility of undesired side reactions under the epimerization conditions discussed above should be addressed. It is possible that the chlorine of the vinyl ether units in the copolymer could have been involved in an undesired side reaction such as dehydrohalogenation or nucleophilic displacement. That such reactions were not the cause of the observed changes in the carbonyl region of the $^{13}C$ NMR spectra upon epimerization was verified by epimerizing an NPM–ethyl vinyl ether (EVE) copolymer. The same changes in the carbonyl region were noted.

In summary, NPM–CEVE copolymers possess predominantly cis stereochemistry at the succinimide units. The ratio of the areas of the copolymer carbonyl peaks appearing at 176.4 and 177.1 ppm (carbon 1) is related to the ratio of trans to cis succinimide units, respectively. The ratio of cis to trans succinimide units depends on the initial mole fraction of NPM in the feed.

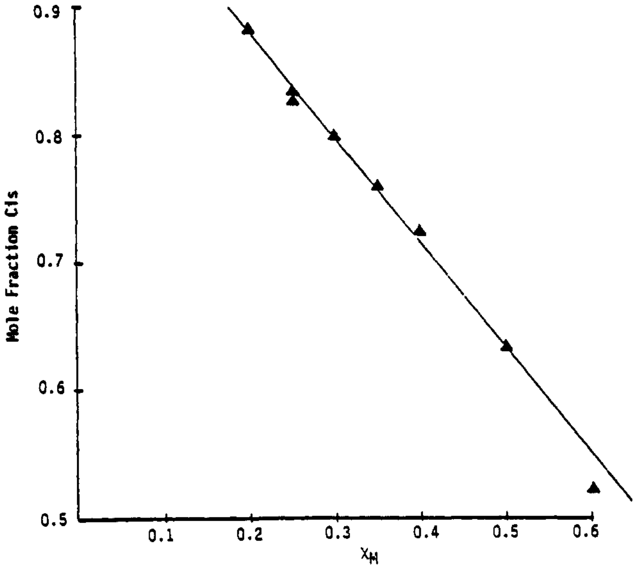


**Figure 11.** Mole fraction of cis succinimide units in NPM–CEVE copolymers vs. $\chi_M$ (constant $M_T$ = [NPM] + [CEVE] = 0.5).

This latter effect was quantified by measuring the relative areas of the two peaks (177.1 and 176.4 ppm) for copolymers prepared at various $\chi_M$'s and expressing the result as the mole fraction cis succinimide units in the copolymers [area(cis)/(area(cis) + area(trans))]. The regularity of the change in this parameter with $\chi_M$ is exhibited by the linear relationship shown in Figure 11. This change may be contrasted with that illustrated in Figure 1 as further evidence that the observed changes are not due to sequence variations. The fact that more cis succinimide units result in copolymers prepared from vinyl ether rich feeds (small $\chi_M$) is significant. If comonomer complexation is viewed as a simple equilibrium, then the fraction of maleimide in complexed form is greater when the vinyl ether is in excess. If the stoichiometry of the complex is 1:1, the equilibrium constant for complex formation, $K$, is related to complex concentration, $C$, maleimide concentration, $A_0$, total monomer concentration, $M_T$, and mole fraction of maleimide, $\chi_M$, as shown in eq 1.[14]

$$C/A_0 = KM_T(1 - \chi_M) \qquad (1)$$

If the polymer stereochemistry at the succinimide units is proportional to the fraction of maleimide that is complexed ($C/A_0$), then the linear relationship shown in Figure 11 is predicted by eq 1. Thus, it is strongly indicated that comonomer complexation has an effect on copolymer stereochemistry.

It is prudent at this juncture to discuss the possible errors in using $^{13}C$ NMR for quantitative studies on polymers. When $^{13}C$ NMR is used for quantitative comparisons, it is important to account for any differences in the spin–lattice relaxation times ($T_1$) and NOE in the resonances being compared. If such differences exist, then the determination of relative areas is likely to be in error.[33,34] Polymers are generally "well behaved", in that $T_1$ and NOE values may vary considerably from one carbon type to another[34,40,41] (see Table I). It is generally recommended[33,34] that if $^{13}C$ NMR is to be used for quantitative purposes, the pulse delay (PD) should be at least 5 times the longest $T_1$ in the sample (>99% relaxation before the next pulse). Due to the number of scans necessary to obtain polymer spectra, the time requirement for the use of such a long PD was prohibitive (e.g., the longest $T_1$ in Table I is 2.5 s; thus, 5 × 2.5 s × 25 000 scans ≅ 87 h). The

PD's used to obtain copolymer spectra were typically 0.180–0.360 s, as compared to the $T_1$ values of about 1.5–2.0 s determined for the carbonyl carbons. Nevertheless, if the $T_1$ values for all of the peaks in the carbonyl region are similar, their relative areas should be comparable. Such behavior is often assumed[40] in polymer $^{13}C$ studies; however, polymer $T_1$'s that are dependent on stereochemical sequences have been reported.[41,50] An experiment was performed on an NPM–CEVE copolymer in which a series of $^{13}C$ spectra was obtained with different pulse delays varying in the range 0.1–2.0 s. No change in the relative intensities of the carbonyl peaks at 177.1 and 176.4 ppm was observed over the range of pulse delays used. It was therefore concluded that there is no significant difference between the $T_1$'s for carbonyls (number 1 in Figure 3) in cis succinimide units as opposed to those in trans units. The relative areas of these peaks thus reflect the relative amounts of cis and trans succinimide units in the copolymers, even though the PD used to obtain the copolymer $^{13}C$ spectra discussed in this work was not 5 times the $T_1$ of the carbon in question. It is also noteworthy that all $^{13}C$ spectra that are compared quantitatively in this work were obtained by using the same PD (360 ms), temperature (110 °C), and solvent ($Me_2SO$-$d_6$).

**Effect of Copolymerization Conditions on Copolymer $^{13}C$ NMR Spectra.** In order to further probe the possibility that copolymer stereochemistry is dependent on the addition of a comonomer complex, a series of copolymerizations was carried out under various initial conditions that would be expected to shift the complex equilibrium one way or the other. The stereochemistry of the resulting copolymers was then investigated by using $^{13}C$ NMR. The effect of the initial mole fraction of maleimide ($\chi_M$) on copolymer stereochemistry has already been discussed.

**Effect of Total Monomer Concentration on Copolymer Stereochemistry.** An increase in the total monomer concentration should shift the above equilibrium to the right and thereby increase the concentration of the complex. Dilution of the reaction mix would be expected to cause the opposite effect. The stereochemistry of NPM–CEVE copolymers also depends on the total monomer concentration. The mole fractions of cis succinimide units are 0.855 for $M_T = 1.77$ and 0.725 for $M_T = 0.5$. Other conditions used to synthesize the copolymers were exactly the same (60.0 °C, AIBN, $\chi_M = 0.4$, $CH_2Cl_2$).

If the copolymer stereochemistry depends on the fraction of maleimide that is complexed, then the increase in the mole fraction of cis succinimide units with $M_T$ observed is predicted by eq 1. The observed increase in stereoselectivity with $M_T$ is hard to rationalize if the "free monomer" mechanism is operational. The higher overall rates of copolymerization commonly observed at higher total monomer concentrations[5] might lead to the expectation of less selectivity and a more random stereochemistry.

**Table II**
**Mole Fraction of Cis Succinimide Units in NPM–CEVE Copolymers Prepared at Various Temperatures[a]**

| $\chi_M$[b] | copolymerization temp, °C | mole fraction of cis succinimide units |
|---|---|---|
| 0.1 | −78 | 0.92 |
| 0.5 | ~25 ± 5 | 0.79[c] |
| 0.5 | 60.0 | 0.69 |
| 0.45 | 100 ± 1 | 0.69[d] |
| 0.3 | ~25 ± 5 | 0.84 |
| 0.3 | 60.0 | 0.80 |
| 0.4 | ~25 ± 5 | 0.86[c] |
| 0.4 | 60.0 | 0.73 |
| 0.6 | ~25 ± 5 | 0.72[c] |
| 0.6 | 60.0 | 0.52 |

[a] Copolymerization conditions: [CEVE] + [NPM] = 0.5, $CH_2Cl_2$, AIBN, 60 °C. [b] Mole fraction of NPM in the initial monomer feed. [c] Areas measured planimetrically. [d] Total monomer concentration = 0.55.

**Effect of Copolymerization Temperature on Copolymer Stereochemistry.** Temperature is also expected to perturb the complex equilibrium. Weak complex formation is generally slightly exothermic and disfavored entropically ($-\Delta H \cong$ 1–10 kcal/mol, $-\Delta S \cong$ 2–20 cal/(mol K)).[51] An increase in temperature would thus be expected to decrease the complex concentration. The stereochemistry of NPM–CEVE copolymers is also temperature dependent. The effect of temperature on copolymer stereochemistry is shown in Table II. It can be seen from Table II that lower copolymerization temperature invariably produces a more stereoregular copolymer. Lower temperature is also expected to lead to a higher equilibrium constant for complex formation ($K$).[51,52] Therefore, if copolymer stereochemistry depends on the fraction of maleimide that is in complexed form, eq 1 predicts that an increase in $K$ will lead to an increase in copolymer stereoregularity.

It should be kept in mind that the configuration of conventional free radically initiated polymers is also temperature dependent,[47] with syndiotactic placements being favored in polymers produced at lower temperatures. This is due to the additional enthalpy of activation required for isotactic placements. The temperature studies described here suggest that the enthalpy of activation is greater for production of trans stereochemical placements at the succinimide units in NPM–CEVE copolymers than it is for cis placements. Trans placements, however, are expected to be thermodynamically favored because of steric repulsion of the alkyl substituents (polymer chains in this case) in cis succinimide structures. Equilibrium epimerization of *cis*-dimethyl-*N*-phenylsuccinimide with 2,2,6,6-tetramethylpiperidine in $Me_2SO$ led to an excess of the trans isomer. This finding supports the above contention. Consecutive alternate addition of "free" comonomers, or a mechanism involving fragmentation of the complex in the transition state, would logically be expected to produce an excess of the more stable trans placements at the succinimide units. This follows from both thermodynamic considerations and the expectation of some steric hindrance to monomer approach from the side of the radical chain end cis to the polymer chain (higher enthalpy of activation). For these reasons, the temperature dependence of copolymer stereochemistry may indicate that a comonomer complex is involved in the propagation steps of NPM–CEVE copolymerization.

**Effect of Copolymerization Solvent on Copolymer Stereochemistry.** The equilibrium constant for DA complex formation ($K$) is generally highly solvent dependent.[13,51] The equilibrium can be perturbed if one or both of the complex participants is strongly solvated. In other words, $K$ depends on the relative strengths of donor–acceptor interactions, donor–solvent interactions, and acceptor–solvent interactions. Copolymers prepared in different solvents exhibited widely varying stereochemistry. This effect is shown in Table III, which includes the $\chi_c$ values for NPM–CEVE copolymers prepared under similar conditions except for solvent. Since benzene is known to form complexes with NPM,[53] the results may be explained as being due to a competition between benzene solvent and CEVE monomer for the acceptor NPM. The overall concentration of NPM–CEVE complexes would thus be

Table III
Effect of Solvent on the Mole Fraction of Cis Succinimide Units in NPM-CEVE Copolymers

| solvent | mole fraction of cis succinimide units ($\chi_c$) |
|---|---|
| none[a] | 0.85[c] |
| benzene[b] | 0.51[c] |
| $CH_2Cl_2$[b] | 0.63 |

[a] Copolymerization conditions: $\chi_M$ = 0.5, AIBN, 60 °C. [b] Copolymerization conditions: $M_T$ = 0.5, $\chi_M$ = 0.5, AIBN, 60 °C. [c] Peak areas estimated by peak intensities.

Table IV
Mole Fraction of Cis Succinimide Units ($\chi_c$) in Various N-Substituted Maleimide-CEVE Copolymers[a]

| maleimide N-substituent | $\chi_c$ | $\sigma$[b] | $K\epsilon^{295c}$ | $10^{-4}K_s$, $M^{-2}$ $cm^{-2}$ |
|---|---|---|---|---|
| $p$-$C_6H_4CN$ | 0.83 | 0.66 | 19.8 | 9.90 |
| $p$-$C_6H_4CF_3$ | 0.78 | 0.54 | 17.0 | 8.50 |
| $p$-$C_6H_4CO_2Et$ | 0.75 | 0.45 | | |
| $p$-$C_6H_4F$ | 0.69 | 0.02 | | |
| $p$-$C_6H_4Cl$ | 0.75 | 0.227 | 15.6 | 7.80 |
| $p$-$C_6H_4Br$ | 0.75 | 0.232 | | |
| $-C_6H_5$ | 0.63 | 0.00 | 13.6 | 5.98 |
| $p$-$C_6H_4OAc$ | 0.65 | 0.31 | | |
| $p$-$C_6H_4CH_3$ | 0.65 | −0.170 | | |
| $p$-$C_6H_4OCH_3$ | 0.60 | −0.268 | 11.3 | 4.97 |
| $-C_6H_{11}$ | 0.63 | | 15.8 | 5.85 |

[a] Copolymerization conditions: [maleimide] + [CEVE] = 0.5, $\chi_M$ = 0.05, 60.0 °C, $CH_2Cl_2$, AIBN. [b] Hammett $\sigma$ constants, taken from ref 14. [c] Determined spectroscopically in $CH_2Cl_2$.

expected to be reduced, causing a decrease in copolymer stereochemistry.

**Effect of Donor and Acceptor Strength on the Stereochemistry of Maleimide–Vinyl Ether Copolymers.** The equilibrium constant $K$ is a measure of the strength of the comonomer donor–acceptor interaction and therefore is expected to vary with the comonomer pair. In order to investigate the effect of the magnitude of $K$ on copolymer stereochemistry, a series of N-substituted maleimides was synthesized and copolymerized with CEVE under similar conditions ($M_T$ = 0.5, $\chi_M$ = 0.5, $CH_2Cl_2$, AIBN, 60.0 °C). The mole fractions of cis succinimide units in these copolymers, along with appropriate Hammett $\sigma$ constants for the N-para-substituted maleimides used, are shown in Table IV. Within the series of N-para-substituted aryl maleimides studied, a fairly good correlation exists between the electron-withdrawing ability of the para substituent (as measured by the Hammett $\sigma$ constant) and $\chi_c$, which is shown in Figure 12. The strength of the interaction between several of the maleimides studied and CEVE was studied spectroscopically in $CH_2Cl_2$ solvent. The absorption spectra of the maleimides studied are shown in Figure 13.

The classical method for the determination of the equilibrium constant for DA formation is that of Benesi and Hildebrand[54] or some modification of it such as the Scott[55] or the Scatchard[56] method. (For a general discussion of these methods, see ref 12, 15, 58, and 59.) The form of the Benesi–Hildebrand equation which has been shown to be applicable to the type of systems being studied is shown in eq 2.

$$A_c = D_0A_0Kl\epsilon \qquad (2)$$

Mixtures of N-substituted maleimides and CEVE exhibited an enhanced absorption in the 255–300-nm region of their UV spectra not present in the spectra of either component alone. This enhanced absorption is believed to be indicative of the formation of a DA between the comonomers. Examination of the charge-transfer band below 245–255 nm proved to be impossible due to strong absorptions by both monomers and solvent in this region. Overlap of the charge-transfer band with absorbances due to both monomers necessitated the use of a subtraction technique in order to obtain values of the absorbance due to complex ($A_c$) at various wavelengths.

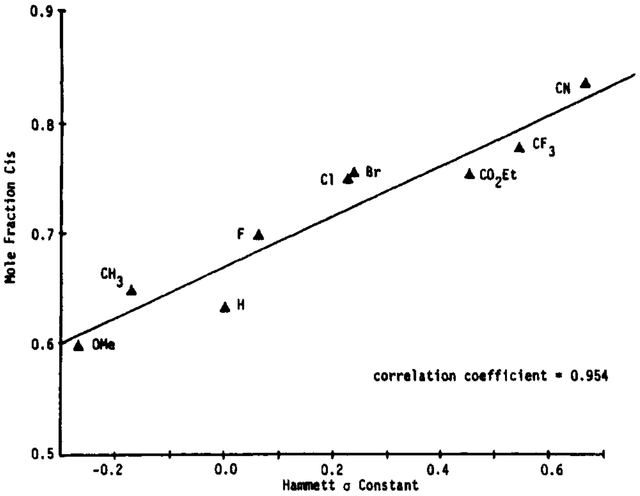


Figure 12. Mole fraction of cis succinimide units in *N*-arylmaleimide–CEVE copolymers vs. Hammett $\sigma$ constant.

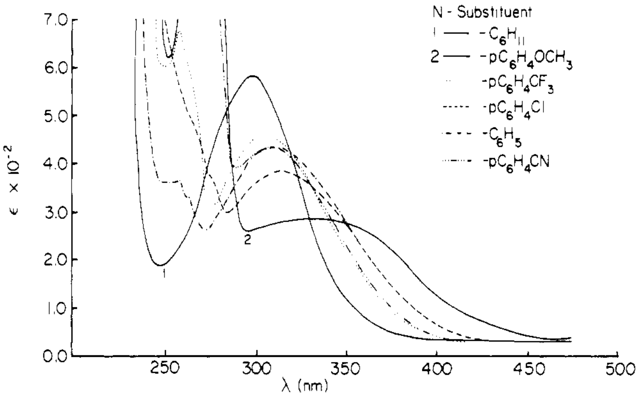


Figure 13. Electronic absorption spectra of various N-substituted maleimides in dichloromethane.

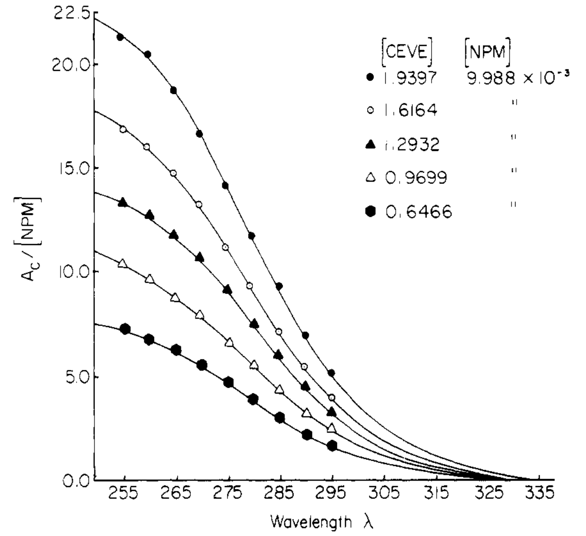


Figure 14. Effect of varying CEVE concentration on the intensity of the NPM–CEVE charge-transfer band.

The intensity of the charge-transfer band was measured for at least five different CEVE concentrations for each maleimide. Invariably, the intensity of the band increased linearly with [CEVE] at all wavelengths. The results for the NPM–CEVE complex are shown in Figure 14. In such cases, $KD_0 \ll 1$, and eq 2, which predicts a linear dependence of $A_c$ on $D_0$ (at constant $A_0$), applies. This means that either $K$ is small or the range of donor concentrations used was not large enough. Unfortunately, higher CEVE concentrations were not practical in this study because CEVE absorbs in the same region as the complex. Only the product $K\epsilon$, and not their separate values, can be determined when such a linear dependence is observed.[59] Therefore, eq 2 predicts that a plot of $A_c/A_0l$ vs. $D_0$ will have a slope of $K\epsilon$.

Absorbance measurements were considered to be least subject to error at 295 nm because the CEVE was nearly transparent at this wavelength, and none of the maleimides exhibited extremely intense absorptions at 295 nm. The slope of a plot of $A_c^{295}/([\mathrm{M}] \times l)$ vs. [CEVE] gives the relative sensitivity of the complex absorption to changes in [CEVE]. The slopes are equivalent to the product of the equilibrium constant for complex formation and the extinction coefficient of the complex at 295 nm ($K\epsilon^{295}$)[58,59] and are given in Table IV.

The present study indicates that the complexation between N-substituted maleimides and CEVE is weak, since the values of $K\epsilon^{295}$ determined are in the range 11–20. The weakness of the interaction also follows from the observation of linearity of the $A_c$ vs. [CEVE] plots over the range of [CEVE] studied, which means $K[\mathrm{CEVE}] \ll 1$ (vide supra). Since the maximum [CEVE] used was about 2 M, $2K \ll 1$ or $K \ll 0.5\ \mathrm{M}^{-1}$.

The $\epsilon^{295}$ value may be small, since the complex absorptions were determined at 295 nm, while the maximum absorption was typically at shorter wavelengths (≤255 nm). The values may be small even at the $\lambda_{\max}$ for the complex, if an analogy can be drawn with the citraconic anhydride–CEVE complex. The value of $\epsilon$ for this system has been determined as 252 L mol$^{-1}$ cm$^{-1}$,[60] compared to the value of 604 L mol$^{-1}$ cm$^{-1}$ [60] determined for the citraconic anhydride–ethyl vinyl ether system. Kokubo et al.[61] studied the complexation behavior of maleic anhydride and CEVE in chloroform. These authors determined a value of 33 L mol$^{-1}$ cm$^{-1}$ for $\epsilon$ at 340 nm ($K = 0.105$, 30 °C) as compared to the value of 690 L mol$^{-1}$ cm$^{-1}$ determined for $\epsilon$ at 350 nm for the *p*-dioxane–maleic anhydride system. Thus, a small extinction coefficient seems to be typical of CEVE complexes. Several groups have also stated that no complexation was evident for *N*-aryl substituted maleimide–donor monomer systems. For example, Barrales-Rienda et al.[62] found no evidence of a charge-transfer band in solutions of NPM and styrene in benzene or cyclohexane. Oishi has also reported that no charge-transfer transitions were observable in the UV spectra of styrene–*N*-(substituted phenyl)citraconimide,[63] and styrene–*N*-alkylcitraconimide[64] solutions. These observations may indicate that $\epsilon$ is small; but even if $\epsilon \leq 100$, the $K$ values would be in the range 0.11–0.17, indicating a weak complexation between the maleimides being studied and CEVE.

The observation of a small equilibrium constant ($K$) for DA formation does not necessarily exclude the complex as a reaction intermediate. Similar linear dependencies of complex absorption on the concentration of added donor have been observed for a number of donor–acceptor systems in a series of recent papers by Fukuzumi and Kochi.[65] Even though these linear dependencies exist, the authors have also provided convincing evidence that the complex is an actual intermediate in many of the reactions studied.

Fukuzumi and Kochi[66] have also defined a parameter $K_s$ to be a measure of the strength of a weak DA as

$$K_s = (1/2)\epsilon_{\max} K \Delta\nu_{1/2} \qquad (3)$$

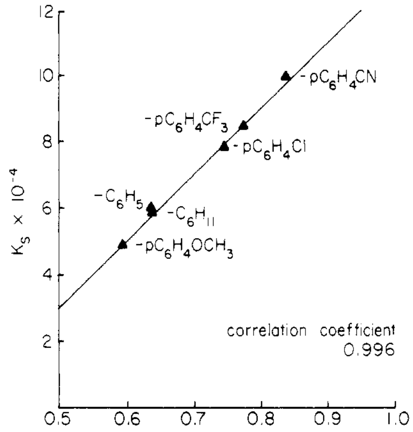


**Figure 15.** Correlation between the strength of comonomer interaction ($K_s$) and the mole fraction of cis succinimide units in N-substituted maleimide–CEVE copolymers ($\chi_c$).

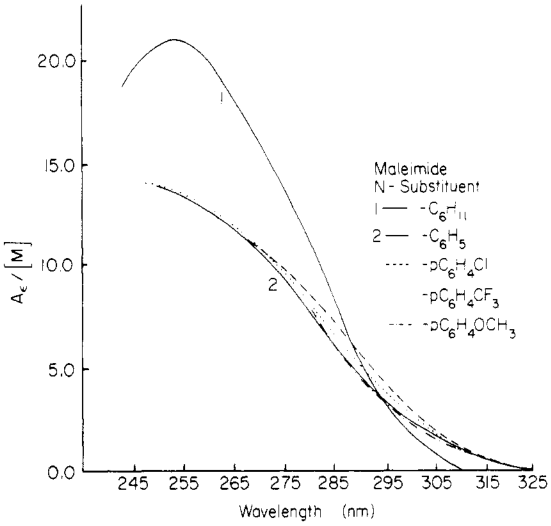


**Figure 16.** Electronic absorption spectra of various N-substituted maleimide–2-chloroethyl vinyl ether charge-transfer complexes; [CEVE] = 1.3 in all cases.

where $\Delta\nu_{1/2}$ is the width of the charge-transfer absorption at half of its maximum height in cm$^{-1}$. Values of $K_s$ for several maleimide–CEVE complexes are also given in Table IV. As can be seen from Figure 15, the mole fraction of cis succinimide units ($\chi_c$) correlates well with the strength of the interaction between the comonomers as measured by the parameter $K_s$. It should be mentioned that the *N*-cyclohexylmaleimide–CEVE charge-transfer band has a definite maximum at 255 nm, but the corresponding maxima for the other maleimides are not evident and must be considered to be ≤255 nm in all cases. Figure 16 shows the normalized absorbance due to the complex (i.e., the absorbance due to the complex [$A_c$], divided by the concentration of maleimide [M]) vs. wavelength ($\lambda$) for the various maleimides studied. The $\Delta\nu_{1/2}$ values used to calculate $K_s$ were thus obtained by assuming that the $\lambda_{\max}$ values for all of the *N*-arylmaleimides were similar (250 nm).

**Effect of the Vinyl Ether Comonomer on the Stereochemistry of NPM–Vinyl Ether Copolymers.** A difference in the donor character of various vinyl ethers may be expected to shift the complex equilibrium and thus effect copolymer stereochemistry. Thus, NPM was copolymerized with CEVE, butyl vinyl ether (BVE), and ethyl vinyl ether (EVE), and the stereochemistry of the resulting copolymers was determined. Similar copolymerization conditions were used in all cases ($M_T = 0.5$,

**Table V**
**Mole Fraction of Cis Succinimide Units in NPM-Vinyl Ether Copolymers**[a]

| vinyl ether | mole fraction of cis succinimide units | $e$[b] |
|---|---|---|
| EVE | 0.75[c] | −1.80 |
| CEVE | 0.63 | −1.58 |
| BVE | 0.51 | −1.50 |

[a] Copolymerization conditions: $M_T$ = 0.5, $\chi_M$ = 0.5, 60.0 °C, $CH_2Cl_2$. [b] Copolymerization polar parameter, taken from ref 66.

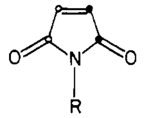
$M$ = 0.5, 60.0 °C, $CH_2Cl_2$), the initiator being AIBN, except in the BVE–NPM copolymerization where 2,4-dichlorobenzoyl peroxide was used.

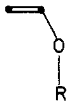
Table V shows that copolymer stereochemistry depends on which vinyl ether comonomer is copolymerized with NPM. The trend in stereoselectivity correlates roughly with the $e$ values, i.e., the most stereoregular copolymer results from copolymerization of NPM with EVE, which is the best donor (as judged by the $e$ value). The NPM–BVE copolymer is the least stereoregular, and BVE has the largest $e$ value in this series.

## Conclusions

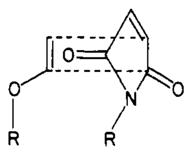
Copolymers of N-substituted maleimides and vinyl ethers exhibit predominantly cis (erythro) stereochemistry at the succinimide units, while the relative stereochemistry between the other chiral centers in the copolymer backbone (vinyl ether–maleimide junction bonds) is essentially random. The stereoselectivity varies with copolymerization conditions in the same way as would be predicted if it were related to the ease of formation of DA complexes between the comonomers.

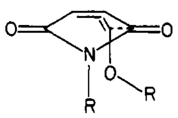
Mulliken theory[13] predicts that the most probable geometry of a DA complex is that in which there is maximum overlap between the HOMO of the donor and the LUMO of the acceptor. The LUMO of maleimide monomers[68] and the HOMO of vinyl ethers are depicted below.



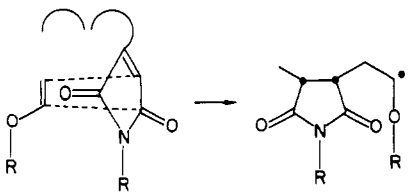


Thus, the expected geometry of the complex may be visualized as





The stereochemical results obtained may be rationalized by invoking attack of the radical chain end on the side of the complex that is syn to the vinyl ether.



This mechanism is, in effect, a concerted addition of the complex to the chain end. The next complex could conceivably add to either side of the vinyl ether radical, thus explaining the random relative stereochemistry between the vinyl ether methine carbon and the methines of adjacent succinimide units observed in the copolymers.

Whether or not a preference for attack by the radical on the more sterically hindered side of the complex is reasonable is open to question. Such a preference for bond formation on the more sterically hindered side of a substrate is not unknown, however. For example, cycloadditions of 1,2,3,4,5-pentachlorocyclopentadiene with various dienophiles lead preferentially to products resulting from addition of the dienophile to the sterically more hindered side of the diene, syn to the 5-chlorine atoms.[69] Jones[70] has found that the cycloadditions of $N$-phenylmaleimide to a 1-hydroxycyclopenta-2,4-diene and the corresponding acetate proceed via exclusive endo addition of the maleimide syn to the hydroxy (or acetate) group. Dienes favoring the syn orientation bear lone-pair electrons on the substituent of the cyclopentadiene ring. Such behavior has been rationalized by Inagaki, Fujimoto, and Fukui[71] as being the result of "nonequivalent extension of the HOMO of the diene". In other words, the HOMO of the diene is biased toward the side of the molecule bearing the heteroatom.

The case at hand may involve the interaction of the singly occupied molecular orbital (SOMO) of the nucleophilic, vinyl ether radical chain end with the lowest unoccupied molecular orbital (LUMO) of the complex (or the LUMO of NPM which has been perturbed on complexation). It is conceivable that the LUMO of NPM is biased in the region syn to the vinyl ether on mixing with the vinyl ether HOMO, thus inducing a preference for attack of the nucleophilic radical syn to the vinyl ether.

It is well-known that vinyl ethers do not readily homopolymerize under free radical conditions,[72] while NPM does homopolymerize under the same conditions used for the copolymerizations described in this paper (see Experimental Section). Thus, it seems unreasonable to postulate a mechanism such as that shown above in which a vinyl ether radical is formed at the chain end on addition of the complex. Also, Iwatsuki et al. have proposed that the complex adds to the chain end in the opposite direction to that proposed here in maleic anhydride–vinyl ether[52,61] and maleic anhydride–anethole[73] copolymerization (i.e., the complex adds so as to form the electrophilic maleic anhydride radical at the chain end). This conclusion was based on the determination of a positive $e$ value for the complex (implying that the radical formed on complex addition was electrophilic). The formation of a maleic anhydride (or maleimide) radical at the chain end on complex addition might also be anticipated, based on the expected radical stabilities of the two possible terminal units. However, a radical $\alpha$ to an oxygen atom is expected to be stabilized by overlap with the filled p-orbitals of the oxygen.[74] Radicals $\alpha$ to oxygen have been observed at 20 °C by electron spin resonance (ESR) spectroscopy.[75] Divinyl ether can be homopolymerized via a free radically initiated cyclopolymerization mechanism, which requires the formation of radicals $\alpha$ to oxygen.[76] Therefore, vinyl ether radicals should be capable of being formed based on the thermodynamic stability of a radical $\alpha$ to oxygen. Indeed, the heat of formation ($\Delta H_f°$) for the $\alpha$ tetrahydrofuryl radical has been reported as −4.3 ± 1.5 kcal/mol, and the $\Delta H_f°$ value of the radical derived from the abstraction of a hydrogen atom from dimethyl ether was found to be −2.8 ± 1.2 kcal/mol.[77]

Therefore, it may be concluded that the reason that vinyl ethers do not homopolymerize free radically is kinetic rather than thermodynamic. It is reasonable that a concerted addition of the maleimide-vinyl ether complex as shown above could considerably lower the energy of activation for the formation of the radical $\alpha$ to oxygen, thus explaining the apparently anomalous results.

The fact also remains that the present stereochemical results could not be explained if the complex adds so as to form a maleimide terminal radical. If a terminal maleimide radical was formed, the more thermodynamically stable trans succinimide unit would be expected to form on addition of the next monomer unit. Similar reasoning may be used to rule out mechanisms involving consecutive alternate addition of "free" monomers, mechanisms involving the concerted addition of the complex followed by fragmentation in the transition state, and mechanisms in which the addition of NPM is reversible.

It is noteworthy that totally alternating copolymers containing all cis succinimide units were obtained only under certain conditions (excess vinyl ether, low temperature). The presence of some trans succinimide units in copolymers prepared under other conditions may indicate that one or more of the above mentioned mechanistic possibilities is also operational. The preponderance of the less thermodynamically stable cis succinimide units in copolymers prepared under conditions expected to favor complex formation may be taken as evidence that the complex cannot be excluded from the reaction coordinate in alternating copolymerizations of maleimides and vinyl ethers.

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**Supplementary Material Available:** Tables giving copolymerization conditions, yields, and analytical data for the copolymers prepared in this study, tables containing kinetic data and rates of polymerization for NPM–CEVE copolymerizations and NPM homopolymerization, and the $^{1}$H NMR, IR, and LRMS data for the monomers and polymers described (15 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) Present address: PPG Industries, Coatings & Resins Division, Allison Park, PA 15101.
(2) Bartlett, P. D.; Nozaki, K. *J. Am. Chem. Soc.* **1946**, *68*, 1495.
(3) Walling, C.; Briggs, E.; Wolfstirn, K.; Mayo, F. R. *J. Am. Chem. Soc.* **1948**, *70*, 1537.
(4) Tsuchida, E.; Tomono, T. *Makromol. Chem.* **1971**, *141*, 265.
(5) Yoshimura, M.; Mikawa, H.; Shirota, Y. *Macromolecules* **1978**, *11*, 1085.
(6) Georgiev, G. S.; Zubov, V. P. *Eur. Polym. J.* **1978**, *14*, 93.
(7) Seiner, J. A.; Litt, M. *Macromolecules* **1971**, *4*, 308.
(8) Karad, P.; Schneider, C. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1137.
(9) Farmer, R. G.; Hill, D. J. T.; O'Donnell, J. H. *J. Macromol. Sci., Chem.* **1980**, *A14*, 51.
(10) Cais, R. E.; Farmer, R. G.; Hill, D. J. T.; O'Donnell, J. H. *Macromolecules* **1979**, *12*, 835.
(11) Hyde, P.; Ledwith, A. In "Molecular Complexes"; Fister, R., Ed.; Paul Elek: London, 1974; Vol. 2.
(12) Dodgson, K.; Ebdon, J. R. *Eur. Polym. J.* **1977**, *13*, 791.
(13) Mulliken, R. S.; Person, W. B. "Molecular Complexes: A Lecture and Reprint Volume"; Wiley-Interscience: New York, 1969.
(14) Olson, K. G.; Butler, G. B. *Macromolecules* **1983**, *16*, 707.
(15) Gordon, A. J.; Ford, R. A. "The Chemist's Companion: A Handbook of Practical Data, Techniques and References"; Wiley: New York, 1972.
(16) Kaufman, M. Postdoctoral Fellow, University of Florida, NIH Grant CA06838.
(17) Vanderbilt, D. P. Ph.D. Dissertation, University of Florida, 1982.
(18) Searle, N. E. U.S. Patent 2444536, July 6, 1948; *Chem. Abstr.* **1948**, *42*, 7340.
(19) Barrales-Rienda, J. M.; Gonzalez Ramos, J.; Sanchez Chaves, M. *J. Fluorine Chem.* **1977**, *9*, 293.
(20) Paraskewas, S.; Lapatsanis, L. *Synthesis* **1979**, 457.
(21) Coleman, L. E.; Bork, J. F.; Dunn, H. *J. Org. Chem.* **1959**, *24*, 135.
(22) Farcasiu, M.; Istratoiu, R. *Rev. Roum. Chim.* **1970**, *15*, 253.
(23) Sakai, T. T.; Dallas, J. L. *FEBS Lett.* **1978**, *93*, 43.
(24) "Deuterated NMR Solvents—Handy Reference Data"; Merck & Co., Inc.: Quebec, 1978.
(25) Ratzsch, M.; Steinert, V. *Acta Polym.* **1980**, *31*, 162.
(26) Froborg, J.; Magnusson, G.; Thoren, S. *J. Org. Chem.* **1975**, *40*, 1595.
(27) Sadtler NMR spectrum no. 14580.
(28) Machida, M.; Machida, M.; Kanaoka, Y. *Chem. Pharm. Bull.* **1977**, *25*, 2739.
(29) Boucherle, A.; Carraz, G. *Bull. Soc. Chim. Fr.* **1960**, *500*; *Chem. Abstr.* **1960**, *54*, 29843a.
(30) Iwatsuki, S.; Itoh, T. *Macromolecules* **1979**, *12*, 208.
(31) Randall, J. C. "Polymer Sequence Determination, Carbon-13 NMR Method"; Academic Press: New York, 1977.
(32) McDonald, G. G.; Leigh, J. S. *J. Magn. Reson.* **1973**, *9*, 358.
(33) Abraham, R. J.; Loftus, P. "Proton and Carbon-13 NMR Spectroscopy, An Integrated Approach"; Heyden and Son Ltd.: London, 1978.
(34) Levy, G. E.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley: New York, 1972.
(35) Olson, K. G.; Butler, G. B. *Macromolecules*, submitted for publication.
(36) Kelen, T.; Tudos, F. *J. Macromol. Sci., Chem.* **1975**, *9*, 1.
(37) Joshi, R. M.; Joshi, S. G. *J. Macromol. Sci., Chem.* **1971**, *A5*, 1329.
(38) Cubbon, R. C. P. *Polymer* **1965**, *6*, 419.
(39) Tawney, P. O.; Snyder, R. H.; Couger, R. P.; Liebrand, K. A.; Stiteler, C. H.; Williams, A. R. *J. Org. Chem.* **1961**, *26*, 15.
(40) Schaefer, J. In "Topics in Carbon-13 NMR"; Levy, G. C., Ed.; Wiley: New York, 1974; Vol. 1.
(41) Heatly, F. In "Progress in NMR Spectroscopy"; Emsley, J. W., Feeny, J., Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, 1979; Vol. 13.
(42) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.
(43) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.
(44) Tonelli, A. E.; Schilling, F. C.; Cais, R. E. *Macromolecules* **1981**, *14*, 560 and references cited therein.
(45) Tonelli, A. E.; Schilling, F. C. *Macromolecules* **1981**, *14*, 74 and references cited therein.
(46) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.
(47) Bovey, F. A. "High Resolution NMR of Macromolecules"; Academic Press: New York, 1972.
(48) Matsuzaki, K.; Ito, H.; Kawamura, T.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 971.
(49) Stowell, J. C. "Carbanions in Organic Synthesis"; Wiley-Interscience: New York, 1979.
(50) Asakura, T.; Doi, Y. *Macromolecules* **1981**, *14*, 72.
(51) Andrews, L. J.; Keefer, R. M. "Molecular Complexes in Organic Chemistry"; Holden-Day, Inc.: San Francisco, 1964.
(52) Iwatsuki, S.; Itoh, T. *Makromol. Chem.* **1979**, *180*, 663.
(53) Bryce-Smith, D.; Hems, M. A. *Tetrahedron* **1969**, *25*, 247.
(54) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
(55) Scott, R. L. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 787.
(56) Scatchard, G. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 660.
(57) Derenleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044.
(58) Foster, R., Ed. "Molecular Association"; Academic Press: London, 1979; Vol. 2.
(59) Person, W. B. *J. Am. Chem. Soc.* **1965**, *87*, 167.
(60) Sharpe, A. J. Ph.D. Dissertation, University of Florida, 1970.
(61) Kokubo, T.; Iwatsuki, S.; Yamashita, Y. *Macromolecules* **1968**, *1*, 482.
(62) Barrales-Rienda, J. M.; Gonzales de la Campa, J. I.; Gonzales Ramos, J. *J. Macromol. Sci., Chem.* **1977**, *A11*, 267.
(63) Oishi, T. *Polym. J.* **1980**, *12*, 799.
(64) Oishi, T. *Polym. J.* **1981**, *13*, 65.
(65) (a) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 2783. (b) Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1981**, *85*, 648. (c) Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1980**, *84*, 617. (d) Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1980**, *84*, 608. (e) Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961.
(66) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1981**, *46*, 4116.
(67) Greenly, R. Z. *J. Macromol. Sci., Chem.* **1980**, *A14*, 427.
(68) Matsuo, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 557.
(69) Williamson, K. L.; Hsu, Y.-F. L. *J. Am. Chem. Soc.* **1970**, *92*, 7385.
(70) Jones, D. W. *J. Chem. Soc., Chem. Commun.* **1980**, 739.

(71) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976,** *98,* 4054.
(72) Field, N. D.; Lorenz, D. H. In "Vinyl and Diene Monomers, Part 1"; Leonard, E. C., Ed.; Wiley-Interscience: New York, 1970.
(73) Kokubo, T.; Iwatsuki, S.; Yamashita, Y. *Macromolecules* **1970,** *3,* 518.
(74) Nonhebel, D. C.; Tedder, J. M.; Walton, J. C. "Radicals"; Cambridge University Press: London, 1979.
(75) Beckwith, A. L. J.; Easton, C. J. *J. Am. Chem. Soc.* **1981,** *103,* 615.
(76) Tsukino, M.; Kunitake, T. *Macromolecules* **1979,** *12,* 387.
(77) O'Neal, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. II, pp 284-285.

# Molecular Structure and Polymerization Mechanism of Poly(vinyl chloride-*co*-carbon monoxide)[1]

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ABSTRACT: Vinyl chloride–carbon monoxide copolymers, prepared by free-radical initiation at 50 °C, are shown to contain the branch structure $-CH_2-CH(COCl)-CH_2-$. This structure could only have arisen from the addition of vinyl chloride to a $-CH_2-\dot{C}H-COCl$ radical that was formed from the $-CH_2-CHCl-\dot{C}O$ radical by a 1,2 halogen shift. The copolymer samples studied were made in bulk or in aqueous suspension under CO pressures ranging from 50 to 845 psi. Following esterification of their COCl groups with methanol, the copolymers were reduced sequentially with $LiAlH_4$ and $Bu_3SnH$, and their $^{13}C$ NMR spectra were then obtained. These spectra revealed the presence of the $-CH_2-CH(CH_2OH)-CH_2-$ branch grouping, together with the cis and trans isomers of 2,4-di(long alkyl)tetrahydrofuran, which evidently had been derived from the $-CH_2-CH(CH_2O^-)-CH_2-CHCl-$ anion by $Cl^-$ displacement. In addition, small amounts of $-CH_2-CH(OH)-CH_2-$ were found, but evidence was obtained to indicate that they had been introduced via air oxidation rather than by copolymerization with carbon monoxide. Methods of synthesis are described for some low-molecular-weight model compounds that were used to obtain the $^{13}C$ shifts of the $-CH_2-CH(CH_2OH)-CH_2-$ structure and the 2,4-di(long alkyl)tetrahydrofurans.

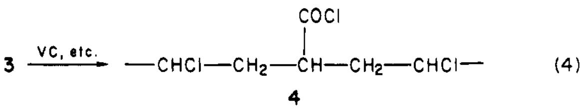
During the past several years, considerable controversy has existed with regard to the molecular structure and polymerization mechanism of the poly(vinyl chloride-*co*-carbon monoxide) (PVC-*co*-CO) that can be prepared by free-radical routes. Kawai and Ichihashi[2] have suggested a conventional mechanism that seems quite reasonable a priori and leads to the formation of structure 2 via reactions 1 and 2. Ratti et al.,[3] on the other hand, have

$$-CH_2-\dot{C}HCl + CO \rightarrow \underset{1}{-CH_2-CHCl-\dot{C}O} \quad (1)$$

$$1 \xrightarrow{\text{VC, etc.}} \underset{2}{-CH_2-CHCl-CO-CH_2-CHCl-} \quad (2)$$

proposed a scheme that is far more intriguing, in that it involves the apparently unprecedented rearrangement[4] (eq 3) of radical 1 into radical 3. Subsequent reaction of 3 with

$$1 \longrightarrow \underset{3}{-CH_2-\dot{C}H-COCl} \quad (3)$$



$$3 \xrightarrow{\text{VC, etc.}} -CHCl-CH_2-\overset{\overset{\displaystyle COCl}{|}}{CH}-CH_2-CHCl- \quad (4)$$

4

vinyl chloride (VC), as in eq 4, should then create a structure, 4, containing a chlorocarbonyl branch.[3] Kawai[2c] and Braun and Wolf[5] have reported chemical and IR evidence which has been stated[2c,5] to establish the presence of 2 in a variety of PVC-*co*-CO samples. However, on the basis of other chemical and spectral findings, Ratti et al.[3] and Braun and Sonderhof[6] have argued for the occurrence of structure 4 instead.

Apart from its intrinsic interest, the PVC-*co*-CO structural problem is important for other reasons. When the free-radical polymerization of vinyl chloride is conducted in the presence of molecular oxygen, carbon monoxide is formed in situ[6,7] and is then removed from the system by copolymerization with vinyl chloride.[6] Small amounts of residual air may remain entrapped in reactors that are used commercially for the preparation of PVC. Thus commercial PVC seems likely to contain low concentrations of adventitious moieties that are identical, structurally, with the oxygen-containing group (or groups) of deliberately synthesized PVC-*co*-CO. Identification of the oxygenated structures in PVC itself has been very desirable for some time in connection with the possible contributions of such structures to the thermal[5-8] and photochemical[5,9] instability of this polymer. Carbonyl-containing structures, in particular, are now attracting much attention in this regard, owing to the recent appearance of several papers in which certain groups of this type are claimed to cause remarkable reductions in the thermal stability of PVC.[8c-e]

Carbon-13 NMR measurements on PVC-*co*-CO are complicated by two problems, viz., the thermal lability of the copolymer under typical analytical conditions and a current lack of reference data for the chemical shifts of interest. In attempting to devise a procedure that would allow these difficulties to be overcome, we envisaged an alternative method involving the $^{13}C$ NMR analysis of PVC-*co*-CO specimens that had been reduced sequentially with lithium aluminum hydride and tri-*n*-butyltin hydride. The $LiAlH_4$ reduction was expected to convert the carbonyl groups of the copolymer into hydroxyl functions, and

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