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Stereochemical Evidence for the Participation of a Comonomer Charge-Transfer Complex in Alternating Copolymerizations

The question of the participation of a comonomer charge-transfer complex in alternating copolymerizations has long been debated. Although considerable data have been amassed over the years, several authors[1,2] have suggested that there has been no unambiguous experimental proof of participation of the complex in the reaction. In order to clarify the mechanism of alternating copolymerization, a new source of data was deemed necessary.

Mulliken theory[3] predicts that maximum amount of charge-transfer stabilization is attained if the conformation of the complex is that 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 comonomer charge-transfer complex adds to the radical chain end in a concerted manner, 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.

Various N-substituted maleimides were shown to copolymerize alternatively with several vinyl ethers. Chloride and nitrogen elemental analysis of *N*-phenylmaleimide (NPM)-2-chloroethyl vinyl ether (CEVE) copolymers prepared by conventional free radical initiation (AIBN, CH_2Cl_2, 60.0 °C) in degassed, sealed tubes indicated that the copolymers contained nearly an equimolar amount of comonomers regardless of the comonomer ratio in the original monomer feed (Figure 1). The NPM–CEVE copolymerization rate (measured gravimetrically) exhibited a maximum at nearly a 1:1 initial comonomer mole ratio, where the comonomer charge-transfer complex concentration would be maximum (Figure 2). Rate profiles such as this are typical of comonomer pairs that polymerize in an alternate manner.[1] Reactivity ratios derived from the composition data by the Kelen–Tüdös[4] method were $r_1 = 0.275$ (NPM) and $r_2 = 0.000$ (CEVE).

Figure 3 shows the ^{13}C NMR spectrum of an 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 (χ_M) = 0.1) in the feed. Copolymers prepared under these conditions possessed totally alternating sequence distributions. The ^{13}C NMR spectra of NPM–CEVE copolymers were found to be markedly dependent on such copolymerization conditions as temperature, initial comonomer ratio, solvent, total monomer concentration, and the relative donor and acceptor strengths of the comonomers. This effect is illustrated in Figure 4, which shows the expanded carbonyl regions of several NPM–CEVE copolymers prepared under similar conditions (AIBN, 60.0 °C, CH_2Cl_2, M_T = [NPM] + [CEVE] = 0.5), except for the initial mole fraction of maleimide in the feed (χ_M). The most obvious variation in these spectra is the change in relative intensity of the peaks at 176.4 and 177.1 ppm from Me_4Si. The upfield peak grows at the expense of the intensity of the downfield peak as χ_M increases. That the aforementioned changes were due to stereochemical differences in the copolymers was established by copolymer epimerization studies. Treatment of solutions of NPM–CEVE copolymers in Me_2SO with 2,2,6,6-tetramethylpiperidine at 60 °C or with potassium *tert*-butoxide at room temperature caused the relative intensities of the carbonyl peaks at 176.4 and 177.1 ppm to change with time. Indeed, the intensity of the peak at 177.1 ppm eventually becomes less than that of the peak at 176.4 ppm. Copolymer epimerization with lithium diisopropylamide in tetrahydrofuran at −78 °C resulted in

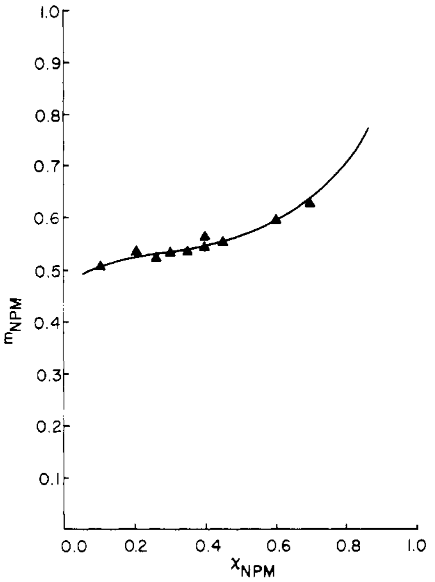


Figure 1. Copolymer composition diagram for the NPM–CEVE system (m_{NPM} = mole fraction NPM in the copolymer, χ_{NPM} = initial mole fraction of NPM in the feed).

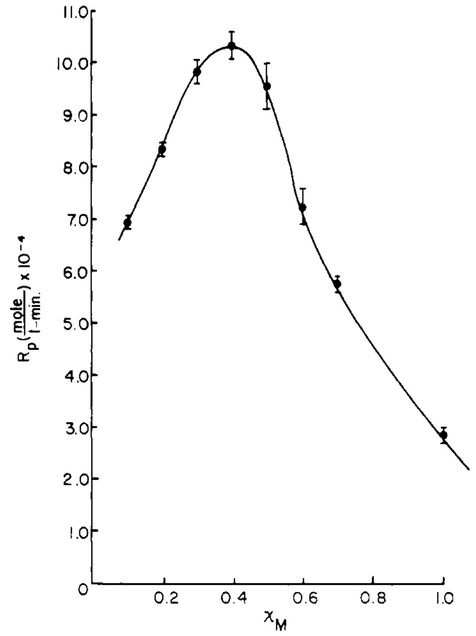


Figure 2. Initial copolymerization rate vs. χ_M for the system NPM, CEVE, AIBN, CH_2Cl_2, 60 °C.

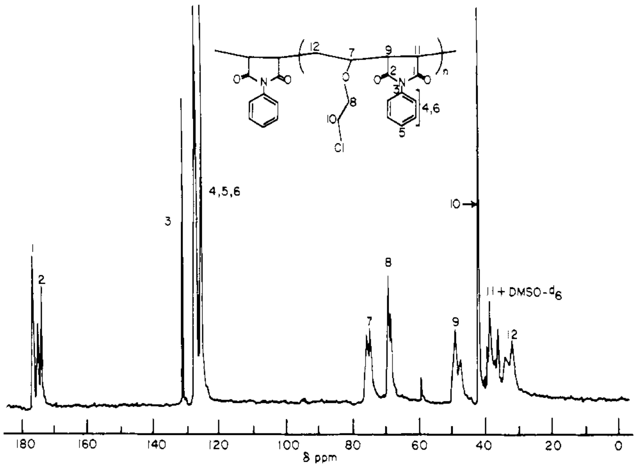


Figure 3. Noise-decoupled ^{13}C NMR spectrum of an NPM–CEVE copolymer, obtained in Me_2SO-d_6 at 110 °C.

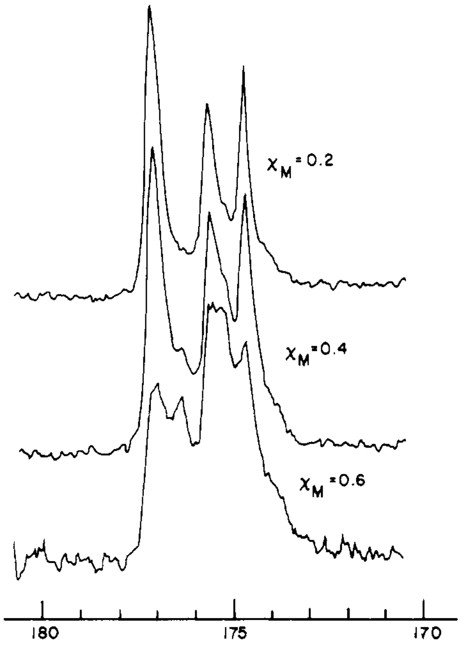


Figure 4. Effect of the mole fraction of NPM in the initial comonomer feed (χ_M) on the appearance of copolymer ^{13}C NMR carbonyl peaks.

nearly equal intensity of the above-mentioned peaks. These results, coupled with the ^{13}C NMR chemical shifts of a series of stereospecific model compounds (Figure 5), suggest that the stereochemistry at the succinimide units in NPM–CEVE copolymers is predominantly cis (erythro). Other model compounds prepared and characterized via ^{13}C NMR were *N*-phenylsuccinimide, *N*-phenyl-*cis*-dimethylsuccinimide, *N*-phenyl-*trans*-dimethylsuccinimide, *N*-phenyl-*cis*-hexahydrophthalimide, and *N*-phenyl-*trans*-hexahydrophthalimide.

The regularity of the change in the relative areas of the ^{13}C NMR carbonyl peaks at 176.4 and 177.1 ppm is illustrated in Figure 6. This change may be contrasted with that illustrated in Figure 1 as further evidence that the observed changes are not due solely to sequence variations.

If comonomer complexation is viewed as a simple equilibrium and the stoichiometry of the complex is 1:1, then the equilibrium constant for complex formation (K) is given by

$$K = C/(A_0 - C)(D_0 - C) \tag{1}$$

where C is complex concentration and A_0 and D_0 are initial concentrations of acceptor (maleimide) and donor (vinyl ether), respectively. If C is small compared to A_0 and D_0, eq 1 is approximated by

$$K = C/A_0D_0 \tag{2}$$

The fraction of maleimide complexed is thus

$$C/A_0 = D_0K = (M_T - A_0)K \tag{3}$$

Expressing A_0 as the mole fraction of maleimide (χ_M) leads to

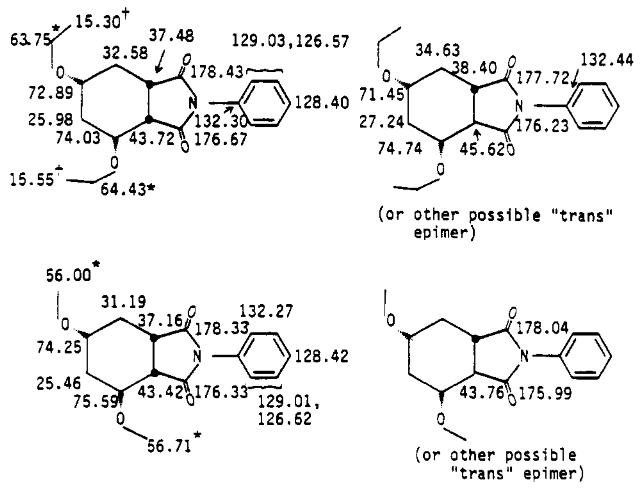
$$C/A_0 = KM_T(1 - \chi_M) \tag{4}$$

If copolymer stereochemistry is dependent on the fraction of maleimide in complexed form, then eq 4 may be expressed as

$$C/A_0 \cong k\chi_c \cong KM_T(1 - \chi_M) \tag{5}$$

where χ_c is the mole fraction of *cis*-succinimide units in the copolymer and k is a proportionality constant. Thus, a linear relationship between χ_c and χ_M such as that shown in Figure 6 is predicted by eq 5.

Equation 5 also predicts that if copolymer stereochemistry is related to the fraction of maleimide in complexed form, then χ_c will be related to both M_T and the equilibrium constant K. In fact, when M_T was increased from 0.500 to 1.77 mol/L ($\chi_M = 0.4$), χ_c also increased from 0.725 to 0.855.



*,† assignments could be reversed

Figure 5. Model compound ^{13}C NMR chemical shifts ($CDCl_3$, ppm from Me_4Si).

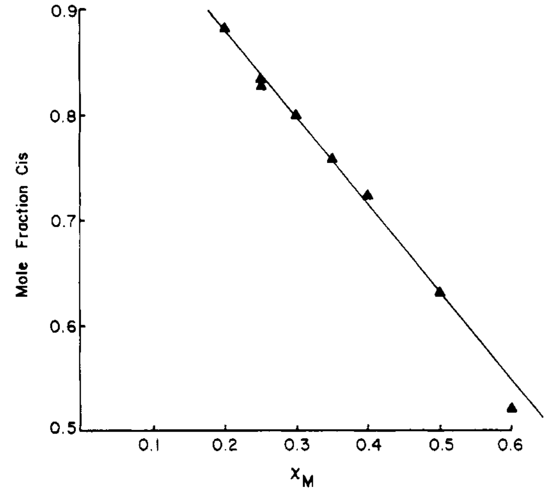


Figure 6. Mole fraction *cis*-succinimide units in NPM–CEVE copolymers vs. χ_M.

Table I
Mole Fraction of *cis*-Succinimide Units in NPM-CEVE Copolymers Prepared at Various Temperatures[a]

χ_M[b]	copolymerization temp, °C	mole fraction *cis*-succinimide units
0.1	−78	0.917
0.5	~25 ± 5	0.785[c]
0.5	60.0	0.685
0.45	100 ± 1	0.690[d]
0.3	~25 ± 5	0.840
0.3	60.0	0.800
0.4	~25 ± 5	0.863[c]
0.4	60.0	0.725
0.6	~25 ± 5	0.717[c]
0.6	60.0	0.521

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

Table II
Mole Fraction of *cis*-Succinimide Units (χ_c) in Various *N*-Substituted Maleimide-CEVE Copolymers[a]

maleimide *N*-substituent	χ_c	σ[b]	$K\epsilon^{295}$ [c]	$10^{-4}K_s$, M^{-2} cm^{-2}
p-C_6H_4CN	0.833	0.66	19.8	9.90
p-$C_6H_4CF_3$	0.776	0.54	17.0	8.50
p-$C_6H_4CO_2Et$	0.752	0.45		
p-C_6H_4F	0.694	0.02		
p-C_6H_4Cl	0.746	0.227	15.6	7.80
p-C_6H_4Br	0.752	0.232		
C_6H_5	0.633	0.00	13.6	5.98
p-C_6H_4OAc	0.649	0.31		
p-$C_6H_4CH_3$	0.649	−0.170		
p-$C_6H_4OCH_3$	0.595	−0.268	11.3	4.97
C_6H_{11}	0.634		15.8	5.85

[a] Copolymerization conditions: [maleimide] + [CEVE] = 0.5, χ_M = 0.05, 60.0 °C, CH_2Cl_2, AIBN. [b] Hammett σ constants, taken from ref 10. [c] Determined spectroscopically in CH_2Cl_2.

The equilibrium constant K is expected to vary with such experimental conditions as temperature, solvent, and the donor–acceptor character of the comonomers. Complex formation is generally exothermic by about 1–10 kcal/mol,[5] so an increase in temperature is expected to decrease the complex concentration. The effect of temperature on copolymer stereochemistry is shown in Table I. In all cases, copolymers prepared at lower temperatures contained a higher fraction of *cis*-succinimide units.

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, χ_M = 0.5, CH_2Cl_2, AIBN, 60.0 °C). The mole fractions of *cis*-succinimide units in these copolymers are shown in Table II. Also shown in Table II are the appropriate Hammett σ constants for tne N-para-substituted maleimides used. Within the series of *N*-(*p*-substituted-aryl)maleimides studied, a fairly good correlation exists between the electron-withdrawing ability of the para substituent (as measured by the Hammett σ constant) and χ_c, which is shown in Figure 7. The mole fraction of *cis*-succinimide units was also shown to increase with the electron donor power of the vinyl ether.

The strength of the interaction between several of the maleimides and CEVE was studied spectroscopically in CH_2Cl_2 solvent. 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 charge-transfer complex between the comonomers. Examination of the charge-transfer complex band below 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^{λ}) at various wavelengths λ. The values of A_c increased linearly with [CEVE] for a series of determinations on solutions of constant [maleimide] and varying [CEVE] ([maleimide] ≪ [CEVE] in all cases). It was not possible to separate the product of the complexation equilibrium constant (K) and the molar absorptivity due to complex (ϵ).[6] However, Fukuzumi and Kochi[7] have defined a parameter K_s to be a measure of the strength of a donor–acceptor complex

$$K_s = \tfrac{1}{2}\epsilon_{max}K\Delta\nu_{1/2} \qquad (6)$$

where $\Delta\nu_{1/2}$ is the width of the CT absorption at half of its maximum height in cm^{-1}. Values of K_s for several maleimide–CEVE complexes are given in Table II. Figure 8 shows that the mole fraction of *cis*-succinimide units (χ_c) correlates well with the strength of the interaction between

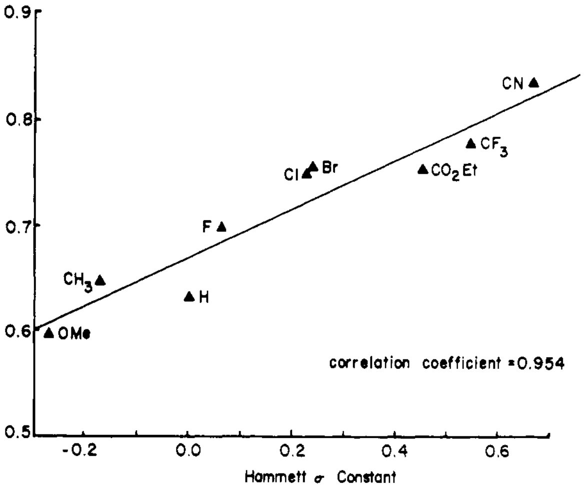


Figure 7. Mole fraction *cis*-succinimide units in *N*-arylmaleimide–CEVE copolymers vs. Hammett σ constant.

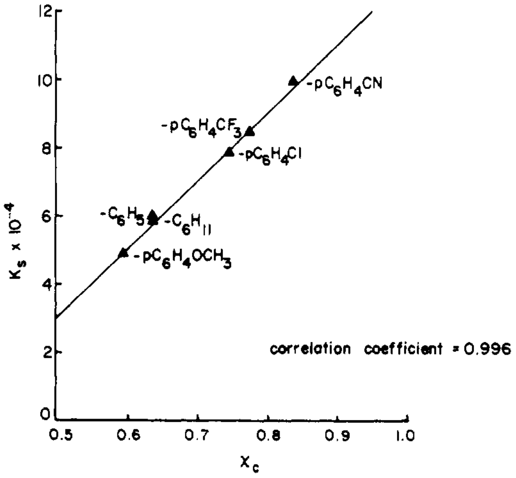


Figure 8. Correlation between the strength of comonomer interaction (K_s) and the mole fraction of *cis*-succinimide units in N-substituted maleimide–CEVE copolymers (χ_c).

Table III
Effect of Solvent on the Mole Fraction of *cis*-Succinimide Units in NPM-CEVE Copolymers[a]

solvent	mole fraction *cis*-succinimide units (χ_c)
none	0.852[b]
benzene	0.505[b]
CH_2Cl_2	0.633

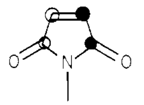
[a] Polymerization conditions: $\chi_M = 0.5$, AIBN, 60 °C. [b] Peak areas estimated by peak intensities.

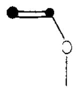
the comonomers, as measured by the parameter K_s.

The equilibrium constant for complex formation is generally solvent dependent.[3] Copolymers prepared in different solvents exhibited widely varying stereochemistry. This effect is shown in Table III, which includes the χ_c values for NPM–CEVE copolymers prepared under similar conditions except for solvent. Since benzene is known to form complexes with NPM,[8] the results may be explained as being due to competition between solvent and CEVE monomer for acceptor NPM. The overall concentration of NPM–CEVE complexes would thus be reduced, causing a decrease in copolymer stereoregularity.

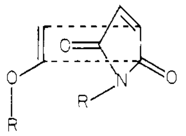
Copolymers of N-substituted maleimides and vinyl ethers have stereochemistry that is predominantly cis (erythro) at the succinimide units, while the relative stereochemistry between the other chiral centers in the copolymer backbone (vinyl ether–maleimide junction bonds) is essentially random. The stereoselectivity varies with such copolymerization conditions as temperature, solvent, total monomer concentration, comonomer concentration ratio at fixed total monomer concentration, and the donor–acceptor character of the comonomer pair in the same way as might be expected if it were related to the ease of formation of charge-transfer complexes between the comonomers.

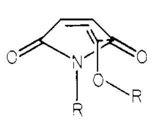
Mulliken theory[3] predicts that the most probable geometry of a charge-transfer complex is that in which there is maximum overlap between the HOMO of the donor and the LUMO of the acceptor. The LUMO of maleimide monomers[9] and the HOMO of vinyl ethers are depicted below.



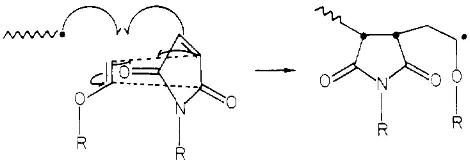


Thus, the expected geometry of the complex may be visualized as





The stereochemical results discussed above 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.

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Registry No. CEVE, 110-75-8; NPM, 941-69-5; *N*-(p-C_6H_4CN)maleimide, 31489-18-6; *N*-(p-$C_6H_4CF_3$)maleimide, 54647-09-5; *N*-(p-$C_6H_4CO_2Et$)maleimide, 14794-06-0; *N*-(p-C_6H_4F)maleimide, 6633-22-3; *N*-(p-C_6H_4Cl)maleimide, 1631-29-4; *N*-(p-C_6H_4Br)maleimide, 13380-67-1; *N*-(p-C_6H_4OAc)maleimide, 6637-46-3; *N*-(p-$C_6H_4CH_3$)maleimide, 1631-28-3; *N*-(p-$C_6H_4OCH_3$)maleimide, 1081-17-0; *N*-(C_6H_{11})maleimide, 1631-25-0.

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Regioselectively Modified Stereoregular Polysaccharides. 6. Synthesis of 3-Deoxy-(1→6)-α-D-*ribo*-hexopyranan[1]

We report a convenient, high-yield procedure for the synthesis of the perfectly 3-deoxygenated linear stereoregular (1→6)-α-D-glucopyranan. According to Scheme I, the free hydroxyl group of 1,6-anhydro-2,4-di-*O*-benzyl-β-D-glucopyranose (**1**) was thioacylated and then reduced with tributylstannane to give 1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose (**3**). Ring-opening polymerization of the deoxygenated monomer **3** in the presence of phosphorus pentafluoride (PF_5) at −60 °C followed by debenzylation yielded 3-deoxy-(1→6)-α-D-*ribo*-hexopyranan (**5**).

Deoxy sugars are biologically important, and several reports[2–4] on chemical syntheses of deoxy polysaccharides via polymerization of 1,6-anhydro deoxy sugar derivatives have recently appeared in succession. Most synthetic procedures of these deoxy monomers, however, are tedious and involve long sequences of reactions. In this paper, we employed the mild deoxygenation method developed by Barton et al.[5–7] and obtained the deoxy compound **3** simply and quickly.

Treatment of **1** with *N*,*N*′-(thiocarbonyl)diimidazole in 1,2-dichloroethane gave 1,6-anhydro-2,4-di-*O*-benzyl-3-