Computer Programs to Study the Charge-Transfer Polymerization Model

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ABSTRACT: Three programs have been written for evaluating the charge-transfer copolymerization model when operating in competition with the terminal model. The first program (program CT-1) permits the calculation of r_1, r_{1c1}, r_{1c2}, r_2, r_{2c2}, r_{2c1}, and K from composition–conversion data. The second program (program CT-2) allows one to design the optimum concentrations of M_1^0 and M_2^0 to use in experimental work. This program may be used sequentially with the first program (and careful experimental work) to ultimately provide the best approach in obtaining r_1, r_{1c1}, r_{1c2}, r_2, r_{2c2}, r_{2c1}, and K. The third program (program CT-3) calculates the copolymer composition, at any conversion, using the charge-transfer model (eq 11) in the most general case. The great importance of using optimum experimental $[M_1^0]$ and $[M_2^0]$ is emphasized. The need for a nonlinear solution is discussed and a nonlinear approach is used which simultaneously permits an objective analysis of the reliability of the method. The sensitivity of predictions to errors in polymer composition and per cent conversion were investigated. Finally, it was demonstrated that no adequate composition–conversion data exist in the literature which can be used to test for a combined-charge-transfer and terminal model copolymerization. The method developed in this paper provides the guide necessary for obtaining such data.

For synthesis and manufacture of copolymers, the copolymer equation has long been the foundation by which their specific composition could be designed.[1,2] Methods used to obtain r_1 and r_2 from composition conversion data include intersection,[3] curve fitting,[3] and linearization techniques (*i.e.*, the Finman–Ross technique[4]) to treat low-conversion copolymerizations. Copolymerizations to higher conversions employed similar methods to fit the integrated form of the copolymer equation.[3,5] Montgomery and Fry[6] provided a computer program to accept composition conversion data at different M_1^0/M_2^0 ratios and converge on r_1 and r_2 at any values of conversion, but the method was inadequate since it did not apply nonlinear least-squares techniques, and it did not define the optimum starting M_1^0/M_2^0 ratios. Many r_1 and r_2 determinations have been summarized in the literature[1,2] using the marginal techniques referenced above.

The importance of using optimum experimental M_1^0/M_2^0 ratios[7] and the mathematical criteria for selecting these conditions[8] requires optimum experimental design and nonlinear solution. One must (1) avoid linearization, and (2) use optimum experimental M_1^0/M_2^0 ratios that minimize the area of the confidence region. To minimize the confidence region[9] it is necessary to choose conditions which minimize the determinant of the variance–covariance matrix.[8] These requirements were largely overlooked until Tidwell and Mortimer[10,11] applied these mathematical criteria to r_1 and r_2 determinations. It is in their method that the basis lies for our approach to analyzing the charge-transfer model using composition–conversion data.

We had employed a similar analyses, previously,[12] to the penultimate copolymerization model[13] which had been used to explain data that did not fit the terminal model.[14-17] However, cases exist where the penultimate model predicted poorly when tested by sequence analysis.[18] Distinction between terminal and penultimate models is very difficult.[18] Attempts to choose among terminal, penultimate, and charge-transfer models must involve extremely careful analysis. If the monomers have similar e values or if the copolymer compositions (or reactivity ratios) are insensitive to dilution, one may usually discard the charge-transfer mechanism.[19] While the sequence distribution approach[20,21] is more sensitive in distinguishing these models,[18] it frequently is more difficult to obtain sequence distribution data. Thus, it remains important that general methods be developed for using optimum composition–conversion data to analyze polymerization models while, simultaneously, permitting an objective analysis of their reliability.

Charge-Transfer Model. The intervention of charge-transfer complexes[22-26] in the propagation sequence often occurs when the two comonomers, M_1 and M_2, vary widely in electron affinity or in their e values (from the Q–e scheme).[1-3] In such cases the monomers can also be in equilibrium with a ground state charge-transfer complex, $M_1 \rightarrow M_2$, hereafter designated as CT.[22,27]

$$M_1 + M_2 \rightleftharpoons CT \qquad (1)$$

$$K_{CT} = [CT]/[M_1][M_2] \qquad (2)$$

When the terminal model is operating, the larger the absolute value between e_2 and e_1 becomes, the greater the tendency to alternation becomes. Similarly, reaction of the polymer chain with a charge-transfer complex gives an alternating structure assuming that $\sim\sim M_1^\bullet$ prefers to add to the M_2 end of CT and that $\sim\sim M_2^\bullet$ adds to the M_1 end of CT.

In the most general case, eight propagation steps could be taking place in a copolymerization where *both* the terminal and charge-transfer mechanisms operate (see eq 3–10). The first four are those of the terminal model, and the last four, to maintain generality, involve the growing polymer chain adding to either end of the CT complex. It would be extremely unlikely that all processes (eq 3–10) would operate, significantly, in a given copolymerization.

$$\sim\sim M_1^\bullet + M_1 \xrightarrow{k_{11}} \sim\sim M_1{-}M_1^\bullet \qquad (3)$$

$$\sim\sim M_1^\bullet + M_2 \xrightarrow{k_{12}} \sim\sim M_1{-}M_2^\bullet \qquad (4)$$

$$\sim\sim M_2^\bullet + M_1 \xrightarrow{k_{21}} \sim\sim M_2{-}M_1^\bullet \qquad (5)$$

$$\sim\sim M_2^\bullet + M_2 \xrightarrow{k_{22}} \sim\sim M_2{-}M_2^\bullet \qquad (6)$$

$$\sim\sim M_1^\bullet + [M_1 \longrightarrow M_2] \xrightarrow{k_{1c1}} \sim\sim M_1{-}M_1{-}M_2^\bullet \qquad (7)$$

$$\sim\sim M_1^\bullet + [M_2 \longleftarrow M_1] \xrightarrow{k_{1c2}} \sim\sim M_1{-}M_2{-}M_1^\bullet \qquad (8)$$

$$\sim\sim M_2^\bullet + [M_1 \longrightarrow M_2] \xrightarrow{k_{2c1}} \sim\sim M_2{-}M_1{-}M_2^\bullet \qquad (9)$$

$$\sim\sim M_2^\bullet + [M_2 \longleftarrow M_1] \xrightarrow{k_{2c2}} \sim\sim M_2{-}M_2{-}M_1^\bullet \qquad (10)$$

Seiner and Litt[28] recently derived a kinetic model, to account for composition–conversion data where both terminal and CT mechanisms compete. Using the usual assumptions of conditional probability and the steady state approximation they derived eq 11 for the most general case,[28]

$$y = \frac{m_1}{m_2} = \frac{\dfrac{1 + \left[\dfrac{r_2}{r_{2c2}} + \dfrac{r_2}{r_{2c1}}\right]\dfrac{[\mathrm{CT}]}{[\mathrm{M}_1]} + \left[\dfrac{r_1}{r_{1c2}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_2]}\right] \left[\dfrac{1 + \dfrac{r_2}{r_{2c2}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_1]}}{1 + \dfrac{r_1}{r_{1c1}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_2]}}\right]}{r_2\dfrac{[\mathrm{M}_2]}{[\mathrm{M}_1]} + 1 + \left[\dfrac{2r_2}{r_{2c2}} + \dfrac{r_2}{r_{2c1}}\right]\dfrac{[\mathrm{CT}]}{[\mathrm{M}_1]} + \left[\dfrac{r_1}{r_{1c2}}\dfrac{\mathrm{CT}}{\mathrm{M}_2}\right]\left[\dfrac{1 + \dfrac{r_1}{r_{2c2}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_1]}}{1 + \dfrac{r_1}{r_{1c1}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_2]}}\right]}}{\dfrac{1 + \left[\dfrac{r_1}{r_{1c1}} + \dfrac{r_1}{r_{1c2}}\right]\dfrac{[\mathrm{CT}]}{[\mathrm{M}_2]} + \left[\dfrac{r_2}{r_{2c1}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_1]}\right]\left[\dfrac{1 + \dfrac{r_1}{r_{1c1}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_2]}}{1 + \dfrac{r_2}{r_{2c2}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_1]}}\right]}{r_1\dfrac{[\mathrm{M}_1]}{[\mathrm{M}_2]} + 1 + \left[\dfrac{2r_1}{r_{1c1}} + \dfrac{r_1}{r_{1c2}}\right]\dfrac{[\mathrm{CT}]}{[\mathrm{M}_2]} + \left[\dfrac{r_2}{r_{2c1}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_1]}\right]\left[\dfrac{1 + \dfrac{r_1}{r_{1c1}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_2]}}{1 + \dfrac{r_2}{r_{2c2}}\dfrac{[\mathrm{CT}]}{[\mathrm{M}_1]}}\right]}} \tag{11}$$

where $r_1 = k_{11}/k_{12}$; $r_{1c1} = k_{11}/k_{1c1}$; $r_{1c2} = k_{11}/k_{1c2}$; $r_2 = k_{22}/k_{21}$; $r_{2c2} = k_{22}/k_{2c2}$; $r_{2c1} = k_{22}/k_{2c1}$; Y = the ratio of M_1/M_2 being incorporated, instantaneously, into the copolymer; $[M_1]$ and $[M_2]$ are the instantaneous concentrations of uncomplexed monomers in solution; CT is the instantaneous concentration of the charge-transfer complex in solution.

Results

Equations 3–10 lead to six reactivity ratios, r_1, r_2, r_{1c1}, r_{1c2}, r_{2c1}, and r_{2c2}, each of which must be known in order to evaluate the initial rate of incorporation of monomers, $d[M_1]/d[M_2]$, into the polymer. As part of our study, 11 was integrated numerically. Equation 11 or its integrated form may be used to determine the six reactivity ratios r_1, r_2, r_{1c1}, r_{1c2}, r_{2c1}, and r_{2c2} provided appropriate composition–conversion data are available. The differential form requires use of very low conversions. After numerical integration of (11), any conversion can be employed, but yields below 15–20% are desired so that each experiment has a reasonable high weighting value. Given sufficient composition–conversion data, these reactivity ratios should be determined by a *nonlinear least-squares* fitting technique that would avoid the mathematical pitfalls which plague linearization techniques.

The desirable method that we employed was the one used for solution of the penultimate effect.[12] Problems facing such computations include (a) defining a unique fit (does such "uniqueness" exist?), (b) avoiding false local minima, (c) defining optimum experimental M_1^0/M_2^0 ratios and concentrations, (d) defining confidence intervals for given data.

Since the [CT] is a function of K_{CT}, the value of K_{CT} could be determined as another parameter in the nonlinear least-squares approach. Alternately K_{CT} could be determined experimentally by uv or (in special cases) by nmr.[22] K_{CT} in each equation might be considered a constant. However, during copolymerization any consideration of K_{CT}, where monomer concentrations are fairly high, raises difficult questions. For example, incorporation of monomers into the polymer will continuously vary bulk solvent properties such as dielectric constant. Thus, K_{CT} is a function of the per cent conversion. Furthermore, changes in solvent properties can cause the extinction coefficient of the complex, ϵ, to change.

Given these complications, rigorous solution of the general problem has been elusive. To date, only a simple case of the general model (*i.e.*, where $k_{22} = 0$) has actually been employed.[28] When this occurs k_{2c2} probably is also 0. In this special (but reasonably common) case, eq 11 is reduced to 12. When $[CT]r_2 \ll [M_1]r_{2c1}$, then θ is very small and

$$y = 1 + \frac{(1/r_{1c1}) + ([M_1]/[CT])}{(1/r_{1c}) + ([M_2]/[CT]r_1)[1 + \theta]} \tag{12}$$

may be neglected. When K_{CT} is small (*i.e.*, K_{CT} 0.03) this should hold since the value of [CT] will be small. Equation 12 now further reduces to eq 13 and only three reactivity ratios plus K_{CT} remain to be determined. Thus, eq 13

$$y = 1 + \frac{(1/r_{1c1}) + ([M_1]/[CT])}{(1/r_{1c}) + ([M_2]/[CT]r_1)} \tag{13}$$

should be applied when $\sim M_2\cdot$ does not add to M_2 and K_{CT} is small.

Charge-Transfer Copolymerization Model Fortran IV Programs. Three programs have been written for the charge-transfer copolymerization model. The first program (program CT-1) permits the calculation of r_1, r_{1c1}, r_{1c2}, r_2, r_{2c2}, r_{2c1}, and K from composition–conversion data. The second program (program CT-2) allows one to design the optimum concentrations of M_1^0 and M_2^0 to use in experimental work. The two programs may be used sequentially (with careful experimental work) to ultimately provide the best approach in obtaining r_1, r_{1c1}, r_{1c2}, r_2, r_{2c2}, r_{2c1}, and K. The third program (program CT-3) calculates the copolymer composition, at any conversion, using charge-transfer model eq 11 in the most general case.

Program CT-1. This program starts with initial estimates of the reactivity ratios (r_1, r_{1c1}, r_{1c2}, r_2, r_{2c2}, r_{2c1}) and K and converges them to the best nonlinear least-squares fit using Marquardt's algorithm.[29,30] It allows for multiple estimates of these parameters to avoid the possibility of falling into a false local minima. This "sector cutting" technique is similar to that employed for the penultimate model.[12] Program CT-1 can employ eq 11, 12, or 13. The user selects the particular case he wishes to use. The user may declare any combination of the parameters (r_1, r_{1c1}, r_{1c2}, r_{2c2}, r_2, K) to be set. If a parameter is set, the program assumes it is correct and does not attempt to change it. This would be useful in a case where K had been determined by separate experiments or where either r_1 or r_2 were known. The parameters are constrained to be greater than zero.

$$\begin{vmatrix} \frac{\partial m_2}{r_1}(M_{1\text{-}1},M_{2\text{-}1}) & \frac{\partial m_2}{r_{1c1}}(M_{1\text{-}1},M_{2\text{-}1}) & \frac{\partial m_2}{r_{1c2}}(M_{1\text{-}1},M_{2\text{-}1}) & \frac{\partial m_2}{K}(M_{1\text{-}1},M_{2\text{-}1}) \\ \frac{\partial m_2}{r_1}(M_{1\text{-}2},M_{2\text{-}2}) & \frac{\partial m_2}{r_{1c1}}(M_{1\text{-}2},M_{2\text{-}2}) & \frac{\partial m_2}{r_{1c2}}(M_{1\text{-}2},M_{2\text{-}2}) & \frac{\partial m_2}{K}(M_{1\text{-}2},M_{2\text{-}2}) \\ \frac{\partial m_2}{r_1}(M_{1\text{-}3},M_{2\text{-}3}) & \frac{\partial m_2}{r_{1c1}}(M_{1\text{-}3},M_{2\text{-}3}) & \frac{\partial m_2}{r_{1c2}}(M_{1\text{-}3},M_{2\text{-}3}) & \frac{\partial m_2}{K}(M_{1\text{-}3},M_{2\text{-}3}) \\ \frac{\partial m_2}{r_1}(M_{1\text{-}4},M_{2\text{-}4}) & \frac{\partial m_2}{r_{1c1}}(M_{1\text{-}4},M_{2\text{-}4}) & \frac{\partial m_2}{r_{1c2}}(M_{1\text{-}4},M_{2\text{-}4}) & \frac{\partial m_2}{K}(M_{1\text{-}4},M_{2\text{-}4}) \end{vmatrix} \tag{14}$$

Program CT-2, Optimum Experimental Conditions. The criterion used to select optimal experimental design was that of finding those initial feed ratios that minimized the area of the confidence region.[7-10] Thus, determinants from eq 11, 12, or 13 were constructed. The user selects the equation he wishes to use and may declare any combination of the parameters to be set. If a parameter is set, the program assumes it is known and does not try to find optimum conditions for that parameter. Since there are three different equations possible and since parameters can be set, the determinant may vary in size from 1 × 1 to 7 × 7. The determinant (eq 14) for eq 13 is 4 × 4 for example. For the charge-transfer model, it is necessary to find two independent variables, ($[M_1]$ and $[M_2]$) for each row of the determinant, *since* $[M_1]$ *and* $[M_2]$ *are concentrations and are independent of each other.*

The determinant (eq 14) assumes no parameters are set. If a parameter is set, the column corresponding to that parameter is eliminated. For instance, if K were set, the last column would be eliminated. The user may set any combination of the independent variables ($[M_1]$ and $[M_2]$). When a variable is set, the program assumes that variable to be an optimum starting concentration and does not change it. Setting one or more of the variables becomes desirable when the determinant becomes larger that about 4 × 4, because the computation time increases by a factor of nine for each additional column and decreases by a factor of three for each variable that is set.

Program CT-3. This program uses eq 11, 12, or 13. After selecting the appropriate equation, the program calculates mole fraction of m_1 and m_2 at any conversion for the charge-transfer model given r_1, r_{1c1}, r_{1c2}, r_2, r_{2c2}, r_{2c1}, K, and the initial concentrations of M_1 and M_2.

Discussion of the Programs

Input–output data are given in Tables I and II. For the case where $k_{22} = 0$ ($r_2 = 0$), eq 13 was employed and a set of sample results are given in Table I. Sample results for the completely general case in (11) are in Table II. Using program CT-1 and eq 13, the composition–conversion data given in columns 1–4 were converged to give the parameters in footnote *a*. Very small perterbations in the polymer compositions did not disturb the ability to converge on a new set of parameters (see footnotes *e* and *g* of Table I). These perterbations are smaller than experiments could detect. Thus, larger perterbations were made. Perterbations of 0.01 or 0.02 will converge on somewhat different values of the reactivity ratios and K. The size of acceptable perterbations depends on: (1) if they are random and (2) the total number of experiments conducted. With random perterbations, larger experimental errors can be tolerated than with systematically biased errors. Given a sufficiently large number of experiments and random perterbations, fairly large experimental errors become acceptable. These are mutually interdependent factors.

Using the values of r_1, r_{1c1}, r_{1c2}, and K given in footnote *a*, the optimum starting concentrations were derived using program CT-2. These are given in columns one and two of Table I. Finally, using the same parameters and the fractional conversions in column three, the polymer compositions in column four were calculated. It is possible to calculate all the parameters simultaneously. However, if the experimental data are not precise, the program may not converge, or it may converge on poor answers. The programs do not take into account any changes in K and/or the concentration of charge-transfer complex due to changes in the solvent properties which occur as the monomer concentrations change. Since optimum experimental conditions call for a wide range of monomer concentrations, this effect is a problem. Currently, the best approach is to handle K as another parameter, rather than assigning it an actual value at a particular set of conditions.[28] It might be possible to determine K experimentally in an exceptional case and the programs can accept an independent K if the user desires.

Next the general case was considered where neither r_1 nor r_2 was zero. Here, all seven parameters (r_1, r_{1c1}, r_{1c2}, r_2, r_{2c2}, r_{2c1}, and K) must be considered and eq 11 employed. To pick a system resembling a real situation, values of r_1 and r_2 were chosen based on calculations from the *Q–e* values of the monomer pair α-chloroacrylonitrile and ethyl vinyl ether.[1] Values of r_{1c1}, r_{1c2}, r_{2c2}, r_{2c1}, and K (see footnote *a* in Table II) were picked realistically based on electronic and steric considerations. Using CT-2 and the chosen values of the parameters, the optimum initial $[M_1{}^0]$ and $[M_2{}^0]$ values were calculated as shown in columns 1 and 2 of Table II. Using these same parameters and the optimum starting concentrations, polymer compositions at the fractional conversions (listed in column 3) were calculated using CT-3. These values of m_2 are listed in column 4. Alternately, using the optimum starting concentrations, given conversions, and given polymer compositions, CT-1 was employed to calculate the value of the reactivity parameters (see footnote *a*). Thus, any user can check these programs with this set of test data.

The sensitivity of the programs to errors in polymer composition was examined. Columns 5 and 6 list biased errors to the high and low side of m_2, respectively. Also alternating data points to the high and low side (balanced error) were examined. Biased data to the high side would not easily converge in a reasonable computer time. However, program CT-1 rapidly converged balanced errors to the values for the parameters shown in footnote *e*. The 95% confidence limits for these calculations were substantial.

It was expedient to first use the Mortimer–Tidwell terminal model program with raw composition–conversion data to get crude values of r_1 and r_2. These serve as the estimates of r_1 and r_2 to feed into CT-1. Alternately, these values plus "sector cutting" could be used. This saves time *vs.* the use of random guesses for r_1 and r_2. The accurate measurement of fractional conversions is quite critical. At initial $[M_1{}^0]$ and $[M_2{}^0]$ of 0.1 and 5.0, respectively, the fraction of M_2 in polymer went from 0.608 to 0.804 as the per

Table I
Input and Output Results for the Charge-Transfer Model for Both "Perfect" and Perturbed Data for Programs CT-1, CT-2, and CT-3[a]

1 Optimum initial $[M_1^0]$[b]	2 Optimum initial $[M_2^0]$[b]	3 Fractional conversion	4 m_2 in polymer[c]	5 m_2 in polymer[d,e]	6 m_2 in polymer[f,g]
5.0	5.0	0.05	0.36107	0.3636	0.3586
5.0	5.0	0.10	0.36233	0.3648	0.3598
5.0	5.0	0.15	0.36367	0.3662	0.3612
5.0	5.0	0.20	0.36511	0.3676	0.3626
5.0	5.0	0.25	0.36665	0.3692	0.3641
0.114	0.106	0.05	0.34491	0.3474	0.3424
0.114	0.106	0.10	0.34651	0.3490	0.3440
0.114	0.106	0.15	0.34818	0.3507	0.3457
0.114	0.106	0.20	0.34994	0.3524	0.3474
0.114	0.106	0.25	0.35179	0.3543	0.3493
5.0	1.1	0.05	0.18131	0.1838	0.1788
5.0	1.1	0.10	0.18104	0.1835	0.1785
5.0	1.1	0.15	0.18077	0.1833	0.1782
5.0	1.1	0.20	0.18051	0.1830	0.1780
5.0	1.1	0.25	0.18026	0.1828	0.1778
0.37	0.1	0.05	0.19558	0.1981	0.1931
0.37	0.1	0.10	0.19589	0.1984	0.1934
0.37	0.1	0.15	0.19622	0.1987	0.1937
0.37	0.1	0.25	0.19692	0.1994	0.1944
0.37	0.1	0.20	0.19656	0.1991	0.1941

[a] Molecular weights: M_1 = 100. M_2 = 100. Parameters: $r_1 = 0.85$, $r_{1c1} = 0.80$, $r_{1c2} = 0.30$, $K = 0.0075$; eq 13 used in calculations. [b] Calculated with program CT-2. [c] Calculated with program CT-3. [d] Values from column 4 have been rounded and 0.0025 added. [e] For these composition data and conversion data of column 3 the parameters calculated by CT-3 are: $r_1 = 0.83$, $r_{1c1} = 0.95$, $r_{1c2} = 0.42$, $K = 0.012$. If K is set at 0.0075 the results are: $r_1 = 0.83$, $r_{1c2} = 0.90$, $r_{1c2} = 0.28$. [f] Values from column 4 have been rounded and 0.0025 subtracted. [g] For the composition data of columns 5 and 6, and the conversion data of column 3, the parameters calculated by CT-3 are: $r_1 = 0.85$, $r_{1c1} = 0.86$, $r_{1c2} = 0.39$, $K = 0.010$. If K is set at 0.0075, the results are: $r_1 = 0.85$, $r_{1c1} = 0.80$, $r_{1c2} = 0.30$.

Table II
Input and Output Results for the Completely General Charge-Transfer Model (eq 11) Using Both Perfect and Perturbed Data in Programs CT-1, CT-2, and CT-3[a]

1 Optimum initial $[M_1^0]$	2 Optimum initial $[M_2^0]$	3 Fractional conversion	4 m_2 in polymer[b]	5 m_2 in polymer[c,e]	6 m_2 in polymer[d]
5.0	5.0	0.05	0.31994	0.32994	0.30994
5.0	5.0	0.10	0.32073	0.33073	0.31073
0.10	5.0	0.05	0.60797	0.61797	0.59797
0.10	5.0	0.10	0.80363	0.81363	0.79363
5.0	1.09	0.05	0.16159	0.17159	0.15159
5.0	1.09	0.10	0.16076	0.17076	0.15076
0.113	0.10	0.05	0.26002	0.27002	0.25002
0.113	0.10	0.10	0.26280	0.27280	0.25280
1.5	2.34	0.05	0.33992	0.34992	0.32992
1.5	2.34	0.10	0.34247	0.35247	0.33247
0.404	5.0	0.05	0.47234	0.48234	0.46234
0.404	5.0	0.10	0.48059	0.49059	0.47059
0.1	2.47	0.05	0.50083	0.51083	0.49083
0.1	2.47	0.10	0.61089	0.62089	0.60089

[a] Molecular weights: M_1 = 100, M_2 = 100 Parameters: $r_1 = 1.7$, $r_{1c1} = 0.1$, $r_{1c2} = 0.3$, $r_2 = 0.0015$, $r_{2c2} = 0.2$, $r_{2c1} = 0.001$, $K = 0.01$. Equation 11 was used in the calculations. [b] Calculated from program CT-3 using given parameters. [c] Values from column 4 have had 0.01 added. [d] Values from column 4 have had 0.01 subtracted. [e] Using the composition data of columns 4 and 5, the following parameters were calculated by CT-1: $r_1 = 1.7$, $r_{1c1} = 0.1$, $r_{1c2} = 0.29$, $r_2 = 0.0015$, $r_{2c2} = 0.18$, $r_{2c1} = 0.0010$, $K = 0.0099$.

cent conversion went from 5 to 10% emphasizing the need for careful experiments (see third and fourth lines of Table II).

Example copolymerizations where eq 13 might be employed include styrene–maleic anhydride, styrene–fumaronitrile, or vinylferrocene–acrylonitrile. In fact, Litt[28] has evaluated several sets of literature data using this approach. *However, it must be emphasized that studies now in the literature were: (1) not performed at the optimum starting concentrations of M_1 and M_2 (indeed for the charge-transfer model these concentrations have never even been rigorously defined), (2) not calculated using nonlinear least-squares methods which appropriately weighted each data point, and (3) not performed with* *sufficient data including enough experiments at the appropriate concentrations, reproducibility studies, and studies testing of the calculated ratios by performing a series of copolymerization experiments at alternate starting concentrations.* When these criteria are met, and only then, should a mechanism involving charge-transfer complexes in competition with the terminal model for composition–conversion data be assigned.

This study demonstrated that no adequate composition–conversion data currently exists in the literature which can be used to test for a combined terminal charge-transfer polymerization model. Second, this technique provides the guide for what experiments should be performed and how many should be conducted. Third, the method requires accurate composition–conversion data. This necessary accuracy surpasses that which is normally obtainable. However, for certain combinations of reactivity parameters, this is less critical than in other regions. Thus, the method discussed above is a first step in the use of composition–conversion data to probe the importance of charge-transfer complexes in copolymerization processes.

Listings of these programs will be made available upon request.

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Motional Phenomena and Multiple Pulse Nuclear Magnetic Resonance. Nonisotropic Motion in Natural Rubber

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ABSTRACT: The nonisotropic nature of the motion in *cis*-polyisoprene, both a natural gum sample and a carbon-filled, sulfur-vulcanized sample, has been investigated by a combination of conventional and multiple pulsed nmr studies of the proton resonance at room temperature. The ability of the multiple pulse techniques to remove residual dipolar broadening from the already partially motionally narrowed proton nmr lines confirms the presence of anisotropic or restricted motion within these materials and an order parameter of 0.006 is determined for the natrual gum sample. A phase altered multiple pulse cycle is used to allow separation of chemical shift information from relaxation effects, and the contribution of chemical shift interactions to the second moment of the free induction decay is determined as well as the relaxation rates. All the protons relax with similar rates in the natural gum sample but exhibit relaxation rates differing by an order of magnitude in the carbon-filled sample; this is attributed to the presence of longer correlation times for the backbone protons in the carbon-filled sample.

One of the most useful measurements in a spectroscopic study is the line shape of the resonance. Particularly in nmr studies of liquids, the line width can be related to relaxation processes in the substance being studied.[1] In solids, however, the dipolar Hamiltonian dominates the line width and little information can be gained from line width studies about the relaxation process or smaller static interactions present.[2] Recent developments in pulse nmr[3–9] have furnished means to reduce greatly, or remove, the effects of the dipolar interaction from solid state nmr spectra and have allowed examination of smaller static interactions, such as the chemical shift tensor.[7] In this paper we illustrate the use of the multiple pulse nmr techniques to separate and characterize spin–spin relaxation processes, chemical shift interactions, and dipolar interactions in solids, particularly in systems where the occurrence of restricted or anisotropic motion complicates any attempt to characterize the motional processes by conventional measurements of the temperature and frequency dependence of spin–lattice relaxation times.[10]

The multiple pulse nmr techniques involve the repetitive application of periodic and cyclic pulse sequences to modify the time development of the spin system. Specific pulse cycles have been developed to reduce the effects of the static dipolar interaction.[3,6,8] However, the presence of molecular motion interferes with the averaging effects of the pulse sequence, and, as the rate of molecular motion increases and approaches the time scale of the pulse se-