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Modelling of the retarded radical polymerization of vinyl acetate in the presence of furan compounds

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The modelling of the retarded radical polymerization of vinyl acetate initiated by 2,2-azobisisobutyronitrile in the presence of furan derivatives was carried out by simulating the monomer concentration and the molecular weight simultaneously. This procedure is based on the method of live and dead moments, which was applied in an original way to the retarded polymerization and permitted the best values of the kinetic parameters for each furan compound to be obtained. Besides, a sensitivity analysis was performed to get a better insight into the mechanism, with the result that degradative transfer is the most important reaction step. The discrepancies observed in the values of the kinetic parameters reported for the unretarded radical polymerization of vinyl acetate lead us to generate 6912 combinations, from which the best estimate that fitted the monomer concentration and the molecular weight was obtained. This set was used to simulate the retarded polymerization. In spite of the mild gel effect observed in unretarded polymerization, it was necessary to include it in order to improve the fitting, particularly if the polymerization was carried out in bulk or at high monomer concentration.

(Keywords: modelling; retarded polymerization; furan derivatives)

INTRODUCTION

The mechanism of retarded radical polymerization has been thoroughly studied, first by Kice[1], Jenkins[2] and Atkinson[3]. Later Deb[4] proposed to include degradative processes with primary radicals. However, the existence of such reactions has not been verified in each system under study. In this context the polymerization of vinyl acetate in the presence of furan compounds has been taken as an example to reach that goal.

The mechanism of retarded or inhibited radical polymerization of vinyl acetate in the presence of furan compounds has previously been studied in a rather limited way by identifying the set of rate constants from initial polymerization rates[5]. This is the so-called inverse problem of chemical kinetics. But this procedure was not useful to obtain a reliable set of rate parameters. Furthermore, two techniques of sensitivity analysis have been carried out to get a better insight into the mechanism of retardation for some furan derivatives[6,7]. Thus, the relative weighting of the macroradical and the primary radical degradative transfers could be compared for the systems under study.

In this paper a thorough modelling study of the retarded polymerization was implemented. Thus, the simultaneous simulation of monomer concentration *versus* time and the molecular weight was carried out using a Gear routine to solve the system of stiff ordinary differential equations. This routine can calculate the live and dead moments for the retardation processes and is coupled with a Simplex algorithm to identify the set of kinetic constants. Furthermore, the sets of rate constants reported for unretarded polymerization of vinyl acetate were checked and a new one is proposed to be used in the simulation of retarded polymerization of this monomer. Also, a sensitivity technique was applied to discriminate the most important reactions of the mechanism for a series of monosubstituted furan derivaties and to obtain a deeper insight into the mechanism.

MODEL EQUATIONS

The complete kinetic mechanism given by Deb[4] for the retardation was assumed, adding transfers with monomer and solvent and termination by coupling and disproportionation. The mechanism includes not only macroradical but primary radical complication:

$$\mathrm{I} \xrightarrow{2fk_\mathrm{d}} 2\mathrm{R}^* \tag{1}$$

$$\mathrm{R}^* + \mathrm{M} \xrightarrow{k_\mathrm{i}} \mathrm{M}_1^* \tag{2}$$

$$\mathrm{M}^* + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{M}^* \tag{3}$$

$$\mathrm{M}^* + \mathrm{M}^* \xrightarrow{k_\mathrm{ta}} \mathrm{P} \tag{4}$$

$$\mathrm{M}^* + \mathrm{M}^* \xrightarrow{k_\mathrm{td}} \mathrm{P}_j + \mathrm{P}_k \tag{5}$$

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$$\mathrm{M^* + M \xrightarrow{k_{trm}} P + m^*} \tag{6}$$

$$\mathrm{M^* + S \xrightarrow{k_{trs}} P + S^*} \tag{7}$$

$$\mathrm{M^* + Z \xrightarrow{k_{trd}} MZ^*} \tag{8}$$

$$\mathrm{MZ^* + M \xrightarrow{k_{is}} M^*} \tag{9}$$

$$\mathrm{MZ^* + M^* \xrightarrow{k_{tc}} P_{\mathit{i}} + P_{\mathit{j}}} \tag{10}$$

$$\mathrm{R^* + Z \xrightarrow{k_{trdp}} RZ^*} \tag{11}$$

$$\mathrm{RZ^* + M \xrightarrow{k_{isp}} M^*} \tag{12}$$

$$\mathrm{RZ^* + M^* \xrightarrow{k_{tcp}} P} \tag{13}$$

The species mass balance equations are developed from the kinetic scheme for the polymeric radical (M*):

$$\frac{\mathrm{d}[\mathrm{M}_1^*]}{\mathrm{d}t} = k_\mathrm{i}[\mathrm{R}][\mathrm{M}] - k_\mathrm{p}[\mathrm{M}_1^*][\mathrm{M}] - k_\mathrm{trm}[\mathrm{M}_1^*][\mathrm{M}] + k_\mathrm{trm}\lambda_0[\mathrm{M}] - k_\mathrm{trs}[\mathrm{M}_1^*][\mathrm{M}] + k_\mathrm{trs}\lambda_0[\mathrm{S}] - (k_\mathrm{ta}+k_\mathrm{td})[\mathrm{M}_1^*]\lambda_0 - k_\mathrm{trd}[\mathrm{M}_1^*][\mathrm{Z}] - k_\mathrm{tc}[\mathrm{M}_1^*]\sum[\mathrm{M}_n\mathrm{Z}^*] \tag{14}$$

$$\vdots \qquad\qquad \vdots$$

$$\frac{\mathrm{d}[\mathrm{M}_n^*]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{M}_{n-1}^*][\mathrm{M}] - k_\mathrm{p}[\mathrm{M}_n^*][\mathrm{M}] - (k_\mathrm{ta}+k_\mathrm{td})[\mathrm{M}_n^*]\lambda_0 - k_\mathrm{trm}[\mathrm{M}_n^*][\mathrm{M}] - k_\mathrm{trs}[\mathrm{M}_n^*][\mathrm{S}] - k_\mathrm{trd}[\mathrm{M}_n^*][\mathrm{Z}] + k_\mathrm{is}[\mathrm{M}_{n-1}\mathrm{Z}^*][\mathrm{M}] - k_\mathrm{tc}[\mathrm{M}_n^*]\sum[\mathrm{M}_n\mathrm{Z}^*] \tag{15}$$

where λ_0 is the total concentration of radical $\Sigma[\mathrm{M}_n^*]$.

For the dead polymer [P]:

$$\frac{\mathrm{d}[\mathrm{P}_n]}{\mathrm{d}t} = k_\mathrm{td}[\mathrm{M}_n^*]\lambda_0 + 0.5k_\mathrm{ta}\sum[\mathrm{M}_{n-m}^*][\mathrm{M}_m^*] + k_\mathrm{trm}[\mathrm{M}_n^*][\mathrm{M}] + k_\mathrm{trs}[\mathrm{M}_n^*][\mathrm{S}] + k_\mathrm{tc}[\mathrm{M}_n^*]\sum[\mathrm{M}_n\mathrm{Z}^*] + k_\mathrm{ptc}[\mathrm{M}_n^*][\mathrm{RZ}^*] \tag{16}$$

For the radical $\mathrm{M}_n\mathrm{Z}^*$ only cross-termination by disproportionation is assumed:

$$\frac{\mathrm{d}[\mathrm{M}_1\mathrm{Z}^*]}{\mathrm{d}t} = +k_\mathrm{trd}[\mathrm{M}_1^*][\mathrm{Z}] - k_\mathrm{is}[\mathrm{M}_1\mathrm{Z}^*][\mathrm{M}] - k_\mathrm{tc}[\mathrm{M}_1\mathrm{Z}^*]\lambda_0 \tag{17}$$

$$\vdots \qquad\qquad \vdots$$

$$\frac{\mathrm{d}[\mathrm{M}_n\mathrm{Z}^*]}{\mathrm{d}t} = k_\mathrm{trd}[\mathrm{M}_n^*][\mathrm{Z}] - k_\mathrm{is}[\mathrm{M}_n\mathrm{Z}^*][\mathrm{M}] - k_\mathrm{tc}[\mathrm{M}_n\mathrm{Z}^*]\lambda_0 \tag{18}$$

To simplify the infinite number of equations into a smaller set, the live (λ_0) and dead moments (μ_0) are introduced[8]:

$$\lambda_k = \sum n^k[\mathrm{M}_n^*] \qquad \mu_k = \sum n^k[\mathrm{P}_n] \tag{19}$$

where n is the degree of polymerization.

Actually only three moments are needed for a reasonable determination of the molecular weight:

$$\overline{M}_\mathrm{n} = \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0} \qquad \overline{M}_\mathrm{w} = \frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1} \tag{20}$$

Finally, the set of differential equations for modelling the retarded polymerization is compacted upon summation (see Appendix).

Molecular weight can be estimated by statistical methods considering chain propagation as a stochastic process. Thus, the probability of propagation[9] is given by:

$$\alpha = \frac{k_\mathrm{p}[\mathrm{M}]}{k_\mathrm{p}[\mathrm{M}] + k_\mathrm{trs}[\mathrm{S}] + k_\mathrm{trm}[\mathrm{M}^*] + k_t\lambda_0} \tag{21}$$

where the transfers with monomer and solvents produce radicals m* and S* (reactions (6) and (7) of the mechanisms) whose reactivy is considered the same as M_1^* because they are not degradative processes.

This probability has been redefined to include hot radical transfer[10] and has worked successfully for the initial conditions of the polymerization. Nevertheless, one has to be careful in extending this approach to retardation or inhibition out of the initial conditions, because the molecular weight is related to the entire history of reaction kinetics. The treatment presented helps to overcome these difficulties.

EXPERIMENTAL

Purifications of 2-furaldehyde (Reachim), 2-acetylfuran (Chemical Sample Co.), 2-furamide (Eastman Kodak), 2-furoic acid (Fluka), 2-furfurylamine (Merck), 2-furfuryl alcohol (BDH), furan (Merck), 2,5-dimethoxy-2,5-dihydrofuran (Pfaltz Bauer), ethyl acetate (BDH) and 2,2′-azobisisobutyronitrile (AIBN; Wako) were carried out by standard techniques. 2-Methylfuran, 2,5-methylfuraldehyde and 2,5-bromofuraldehyde were kindly supplied by the Organic Chemistry Laboratory and also purified by standard techniques and characterized by i.r. and n.m.r. spectra. Vinyl acetate (BDH) was purified by prepolymerization and doubly distilled. Dilatometric determination has already been reported[6].

The molecular weights of polymers were determined by g.p.c. using a HPP 4001 type high-pressure instrument from Czechoslovakia with tetrahydrofuran as solvent at room temperature on PLGel columns (100, 500, 10^3, 10^4, 10^5, 10^6, 10^7 Å). The calibration curve was plotted according to May and Knight[11] using a fifth-degree polynomial.

MODELLING

All programs to model the mechanism of polymerization were written in FORTRAN-77 and implemented for IBM-compatible microcomputer. The minimization algorithm to identify the kinetic constants was the Simplex[12]. Simplex worked fairly well while Levenberg–

Marquardt failed to do so[13], possibly due to the low or zero values of the Jacobian matrix. The simultaneous simulation of monomer concentration *versus* time and the molecular weight was carried out using a Gear algorithm[14] to resolve the stiff system of non-linear first-order ordinary differential equations obtained by using the method of moments.

If only the monomer concentration is fitted, several sets of rate constants were obtained and the variation in some constants is over 2–3 orders. Nevertheless if both monomer concentration and molecular weight are fitted, the variation is less than an order of magnitude.

A brief description of the programs is offered.

SELECONS permits one to obtain a combination of kinetic constants from literature data for the polymerization of vinyl acetate at 60°C in bulk or in ethyl acetate[15–17] that better fits the experimental monomer concentration and the molecular weight for several runs. The program generates 6912 combinations and each set is checked. It is used for the unretarded polymerization.

COGEAR simulates simultaneously the monomer concentration and the molecular weight using the best values of the rate parameters obtained by SELECONS, but it includes the variation of k_t with conversion to take into account the gel effect. It is used for the polymerization without retarder. Thus when applied to retarded polymerization no gel effect is needed to improve the fit as expected for a degradative process.

COSIMGEA can simultaneously change the values of the rate parameters that involve degradative processes using Simplex and resolve the system of ordinary differential equations to simulate monomer concentration and molecular weight. The best rate parameters obtained by SELECONS for unretarded polymerization are supplied and do not change during the run of the programs. The output gives the best estimated parameter for the retarding processes.

SENSICON can calculate all normalized coefficients:

$$\sigma_{ij}=\frac{\partial \ln C_i}{\partial \ln k_j} \tag{22}$$

of the sensitivity matrix by using a direct technique. This technique was already reported and thoroughly discussed[7]. The values of the coefficient permit one to evaluate the influences of each reaction step over the overall kinetics.

RESULTS AND DISCUSSION

Some features of the effect of furan derivatives on the radical polymerization of vinyl acatate

Reactivity of monosubstituted furan compounds is shown in *Table 1*. The initial rate of polymerization (R_{p0}) of vinyl acetate initiated by AIBN increases from 2-furaldehyde to 2-methylfuran, showing the greater stabilization that the carbonyl double bond imparts to the radical formed. On the contrary, disubstituted furans behave as weaker retarders in comparison with 2-furaldehyde owing to the blocking of the carbon C5 position of the ring, as has been suggested already[18]. 2,5-Dihydrofuran must be formed if radical addition occurs on the C5 position. But dihydrofurans formed have no decisive influence on the retardation process as is shown.

Table 1 Retarding effect of furan compounds in the polymerization of vinyl acetate (VA) initiated by AIBN at 60°C[a]

Furan side group	Initial velocity, R_{p0} ($\times 10^5$ mol dm^{-3} s^{-1})
CHO	4
$COCH_3$	9
$CONH_2$	14
COOH	15
CH_2NH_2	31
CH_2OH	37
H	40
CH_3	44
5-Br, 2-CHO	35
5-CH_3, 2-CHO	34
2,5-OCH_3 dihydrofuran	75

[a] [VA] = 8.65 mol dm^{-3}, [AIBN] = 5.0×10^{-3} mol dm^{-3}

The polymerization of vinyl acetate without retarders

The unsatisfactory state of published kinetic parameters for free-radical polymerization, where the same parameter may vary by orders of magnitude, has been pointed out[19]. Vinyl acetate is not an exception in this context.

Thus the set of kinetic constants obtained by SELECONS for the unretarded free-radical polymerization is better than any of the 6912 combinations obtained from published data:

$$f=0.83 \qquad k_d=9.4\times 10^{-6} \qquad k_i=16 \qquad k_p=2500$$
$$k_t=3.0\times 10^7 \qquad k_{trm}=0.70 \qquad k_{trs}=0.82$$

It is interesting to note that the fit is better if k_t is assumed as by disproportionation and not by coupling.

However, the result of the simulation can be improved if the gel effect is taken into account. With this purpose COGEAR permitted one to calculate empirically the possible changes of the termination constant k_t. For the increase of k_t due to the fact that the solvent becomes thermodynamically bad[20]:

$$k_t=k_{t0}+\delta[P]$$
$$k_t=3.5\times 10^7+0.38[P]$$

and for the decrease of k_t due to segmental diffusion control[21]:

$$k_t=k_{t-1}-(K_1[\Delta P]^n K_2 X_w^m)k_{t-1}$$
$$k_t=k_{t-1}-(2.1\times 10^4[\Delta P]^{0.95} X_w^{0.93})k_{t-1}$$

where [ΔP] is the increase in polymer concentration in the interval, k_{t-1} is the decrease of k_t in the interval and X_w the degree of polymerization in weight.

In *Table 2* is shown in a compacted form the results of the molecular-weight prediction and also how the above consideration improves the fitting for the monomer concentration expressed as the mean error in per cent for all experimental points of each run.

Retarded radical polymerization

The program COSIMGEA fits the data of monomer concentration *versus* time and the molecular weight of all kinetic runs for each retarder. The output gives the

Table 2 Simulation of the unretarded radical polymerization of vinyl acetate (VA) in ethyl acetate or in bulk

$[VA]_0$ (mol dm^{-3})	[AIBM] (mol dm^{-3})	Mean error per run (%) in estimation of monomer conc.		Degree of polymerization, $\overline{X}_n$		
		Without gel effect	With gel effect	Obs.	Calc.	Dev. (%)
5.41	5.0×10^{-3}	4.5	3.0	1325	1359	7.5
6.49	5.0×10^{-3}	6.4	1.6	1084	1193	9.1
7.57	5.0×10^{-3}	4.9	2.9	1575	1400	−12.5
8.65	5.0×10^{-3}	2.7	1.9	1995	1842	−8.3
9.72	5.0×10^{-3}	5.3	3.0	2481	2954	16.0
8.65	1.0×10^{-3}	2.9	1.5	2412	2831	14.8
8.65	3.0×10^{-3}	1.2	0.5	2272	2225	−2.1
8.65	5.0×10^{-3}	2.7	1.9	1995	1842	−8.3
8.65	7.0×10^{-3}	3.3	0.8	1967	1800	−9.3

Table 3 Sets of rate parameters obtained for the retarded polymerization of vinyl acatate (VA) initiated by AIBN at 60°C in presence of furan derivatives[a]

Furan side group	Macroradical complication			Primary complication		
	k_{trd}	k_{is}	k_{tc}	k_{trdp}	k_{isp}	k_{tcp}
CHO	4800	1.1×10^{-4}	2.2×10^{8}	8400	0.0012	5.7×10^{8}
$COCH_3$	2600	3.5×10^{-4}	4.7×10^{8}	7700	0.0034	7.5×10^{8}
$CONH_2$	1800	2.4×10^{-3}	5.4×10^{8}	2200	2.0	9.8×10^{8}
COOH	1700	2.6×10^{-3}	5.7×10^{8}	2000	2.0	1.0×10^{9}
CH_2NH_2	720	3.4×10^{-3}	6.3×10^{8}	860	3.7	1.1×10^{9}
CH_2OH	590	5.9×10^{-2}	8.8×10^{8}	760	4.0	1.8×10^{9}
H	510	7.1×10^{-2}	1.4×10^{9}	700	6.1	2.2×10^{9}
CH_3	490	8.1×10^{-2}	2.4×10^{9}	490	8.1	3.1×10^{9}

[a] [VA] = 8.65 mol dm^{-3}, [AIBN] = 5.0×10^{-3} mol dm^{-3}

Table 4 Simulation of the conversion for the radical polymerization of vinyl acetate (VA) at 60°C in presence of furan derivatives[a]

Furan side group	[Retarder] (mol dm^{-3})	Time (min)	Polymerization (%)			Mean error per run (%) in monomer conc.
			Expt.	Calc.	Dev.(%)	
CHO	3.1×10^{-3}	85	2.3	2.3	0.0	0.2
$COCH_3$	2.7×10^{-3}	106	6.1	6.6	8.2	0.2
$CONH_2$	3.0×10^{-3}	115	11.6	11.4	−1.7	0.1
COOH	3.0×10^{-3}	170	17.8	17.3	−2.8	0.3
CH_2NH_2	3.0×10^{-3}	115	25.0	23.9	−4.4	0.4
CH_2OH	2.9×10^{-3}	85	21.5	22.1	2.8	0.6
H	2.9×10^{-3}	85	22.3	23.1	3.6	0.8
CH_3	3.0×10^{-3}	71	20.5	20.2	−1.5	0.2

[a] [VA] = 8.65 mol dm^{-3}, [AIBN] = 5×10^{-3} mol dm^{-3}

Table 5 Simulation of the molecular weight for the radical polymerization of vinyl acetate (VA) at 60°C in presence of furan derivatives[a]

Furan side group	[Retarder] (mol dm^{-3})	Time (min)	Degree of polymerization, $\overline{X}_n$		
			Obs.	Calc.	Dev. (%)
CHO	3.1×10^{-3}	240	591	518	−12.3
$COCH_3$	2.7×10^{-3}	240	856	912	6.5
$CONH_2$	3.0×10^{-3}	120	1050	1131	7.7
COOH	3.0×10^{-3}	240	1193	1144	4.1
CH_2NH_2	3.0×10^{-3}	120	1798	1615	−10.2
CH_2OH	2.9×10^{-3}	240	1430	1593	11.4
H	2.9×10^{-3}	240	1667	1622	−2.7
CH_3	3.0×10^{-3}	240	1687	1621	−3.8

[a] [VA] = 8.65 mol dm^{-3}, [AIBN] = 5×10^{-3} mol dm^{-3}

best set of kinetic constants as shown in *Table 3*. The kinetic constants f, k_d, k_i, k_p and k_t were supplied as the best combination obtained by SELECONS and remained unchanged. The goodness of the fitting is shown in *Tables 4* and *5*.

Several conclusions are drawn from *Table 3*:

(a) Macroradical degradative transfer constants obtained (k_{trd}) have values according to the experimental decreasing retardation power (see *Table 1*) from the strongest, 2-furaldehyde, to the weakest, 2-methylfuran.

(b) Reinitiations are less important for the stronger retarders.

(c) As a rule primary radical transfer constants (k_{trdp}) and cross-termination (k_{tcp}) are greater than k_{trd} and k_{tc}, probably due to the microradical character of R*.

(d) Cross-terminations k_{tc} and k_{tcp} are greater for the weaker retarders.

All these results are chemically compatible.

Sensitivity analysis

The sensitivity matrix was obtained according to the methodology given by Come[22]. This technique has already been described[7].

The matrix was obtained for each retarder and all the results are shown in a compacted form in *Table 6*. Each number represents the sum of the column vector in the matrix corresponding to each retarder. Macroradical degradative transfer is the most sensitive process and the primary radical degradative transfer must be included in the mechanism.

The reinitiation (k_{is}) of the MZ* radical can be ruled out, taking into account the low values (less than one) obtained.

CONCLUSIONS

The radical polymerization of vinyl acetate retarded by furan compounds could be simulated and a reliable set of rate constants for each retarder obtained by fitting simultaneously the monomer concentration and the

Table 6 Results of the sensitivity analysis for the retarded polymerization of vinyl acetate (VA) initiated by AIBN at 60°C in presence of furan derivatives offered in a compacted matrix

Furan side group	Macroradical complication			Primary complication		
	k_{trd}	k_{is}	k_{tc}	k_{trdp}	k_{isp}	k_{tcp}
CHO	179.94	0.02	10.00	4.05	4.04	3.19
$COCH_3$	81.20	0.02	9.99	3.41	3.38	2.50
$CONH_2$	43.69	0.05	9.92	1.20	0.97	0.25
COOH	40.79	0.05	9.92	1.19	0.98	0.24
CH_2NH_2	14.44	0.02	9.91	1.10	0.95	0.12
CH_2OH	11.27	0.18	9.33	1.12	1.03	0.13
H	9.66	0.11	9.40	1.10	1.00	0.12
CH_3	9.34	0.07	9.55	1.07	0.99	0.08

molecular weight using a modified method of moments. The main features of the mechanism were revealed by combining these results with a sensitivity analysis.

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APPENDIX

Rate equations for the mechanism of retarded radical polymerization

$$\frac{d[I]}{dt} = -k_d[I]$$

$$\frac{d[S]}{dt} = -k_{trs}[S]\lambda_0$$

$$\frac{d[R^*]}{dt} = -k_i[R^*][M] + 2fk_d[I] - k_{trdp}[R^*][Z]$$

$$\frac{d[Z]}{dt} = -k_{trd}[Z]\lambda_0 - k_{trdp}[R^*][Z]$$

$$\frac{d\sum[M_nZ^*]}{dt} = k_{trd}[Z]\lambda_0 - k_{is}[M]\sum[M_nZ^*] - k_{tc}\lambda_0\sum[M_nZ^*]$$

$$\frac{d[RZ^*]}{dt} = -k_{trdp}[R^*][Z] - k_{isp}[M][RZ^*] - k_{tcp}\lambda_0[RZ^*]$$

$$\frac{d[M]}{dt} = -k_p\lambda_0[M] - k_{trm}\lambda_0[M] - k_i[M][R^*] - k_{is}[M][MZ^*] - k_{isp}[M][RZ^*]$$

$$\frac{d\lambda_0}{dt} = -k_{trd}\lambda_0[Z] + k_i[R^*][M] + k_{is}[M]\sum[M_nZ^*] - k_{tc}\lambda_0\sum[M_nZ^*] - (k_{ta} + k_{td})\lambda_0^2 + k_{isp}[M][RZ^*] - k_{tcp}[RZ^*]\lambda_0$$

$$\frac{d\lambda_1}{dt} = -k_{trd}\lambda_1[Z] + k_i[R^*][M] + k_{is}[M]\sum n[M_nZ^*] - k_{tc}\lambda_1\sum[M_nZ^*] - (k_{ta} + k_{td})\lambda_0\lambda_1 + k_p[M^*]\lambda_0 - k_{tcp}[RZ^*]\lambda_1 + (k_{trs}[S] + k_{trm}[M])(\lambda_0 - \lambda_1)$$

$$\frac{d\lambda_2}{dt} = -k_{trd}\lambda_2[Z] + k_i[R^*][M] + k_{is}[M]\sum n^2[M_nZ^*] - k_{tc}\lambda_2\sum[M_nZ^*] - (k_{ta} + k_{td})\lambda_0\lambda_2 + k_p[M^*](2\lambda_1 + \lambda_0) - k_{tcp}[RZ^*]\lambda_2 + (k_{trs}[S] + k_{trm}[M])(\lambda_0 - \lambda_2)$$

$$\frac{d\mu_0}{dt} = +k_{trs}\lambda_0[S] + k_{trm}[M]\lambda_0 + k_{tcp}[RZ^*]\lambda_0 + k_{tc}\lambda_0\sum[M_nZ^*] + (0.5k_{ta} + k_{td})\lambda_0^2 + k_{isp}[M][RZ^*]$$

$$\frac{d\mu_1}{dt} = +k_{trs}\lambda_1[S] + k_{trm}[M]\lambda_1 + k_{tcp}[RZ^*]\lambda_1 + k_{tc}\lambda_1\sum[M_nZ^*] + (k_{ta} + \mathrm{k}_{td})\lambda_0\lambda_1$$

$$\frac{d\mu_2}{dt} = +k_{trs}\lambda_2[S] + k_{trm}[M]\lambda_2 + k_{tcp}[RZ^*]\lambda_2 + k_{tc}\lambda_2\sum[M_nZ^*] + (k_{ta} + k_{td})\lambda_0\lambda_2 + k_{ta}\lambda_1^2$$

where

$$\sum[M_nZ^*] = \frac{k_{trd}\lambda_0[Z]}{k_{is}[M] + k_{tc}\lambda_0}$$

$$\sum n[M_nZ^*] = \frac{k_{trd}\lambda_1[Z]}{k_{is}[M] + k_{tc}\lambda_0}$$

$$\sum n^2[M_nZ^*] = \frac{k_{trd}\lambda_2[Z]}{k_{is}[M] + k_{tc}\lambda_0}$$

by applying the steady-state hypothesis.