



Modeling of Superacid Catalyzed Step-Growth Polymerization of Isatin and Biphenyl or Terphenyl Monomers

Juan Enrique Romero-Hernández, Alfredo Cruz-Rosado, Mikhail G. Zolotukhin, and Eduardo Vivaldo-Lima*

A mathematical model for the kinetics and molecular weight development of superacid catalyzed step-growth polymerization of isatin and biphenyl or terphenyl monomers is developed. By considering different reactivities among the several types of polymer molecules present in an otherwise conventional $A_2 + B_2$ step-growth polymerization system, ultrahigh molecular weights are predicted by the model for superacid catalyzed polyhydroxyalkylation reactions, a result that remains unclear in the literature since it seems to be in disagreement with the classical $A_2 + B_2$ theory. Three polymerization systems are addressed in this study: (a) polymerization of isatin and biphenyl, (b) modified isatin and biphenyl, and (c) modified isatin and terphenyl. Overall good agreement between calculated and experimental results of polymerization rate, and evolution of number- and weight-average molecular weights (M_n and M_w , respectively) is observed. However, some discrepancies for molar mass dispersity (\mathcal{D}) are observed.

reactions and found that they can be used in the synthesis of diarylated compounds.

Zolotukhin and co-workers^[3–9] developed a superacid catalyzed polyhydroxyalkylation novel synthetic route (see Figure 2), which can be classified as an unusual $A_2 + B_2$ step-growth polymerization since ultrahigh molecular weights and molar mass dispersities (\mathcal{D}) less or higher than two are possible, at nonstoichiometric conditions. The dramatic acceleration in polymerization rate observed in superacid catalyzed polyhydroxyalkylations with a small excess of the carbonyl compound is known as the “nonstoichiometric effect.”^[6] Superacid catalyzed polyhydroxyalkylations have the following advantages:^[6] (i) the reaction proceeds at room temperature and atmospheric pressure, (ii) structural variety and commercial availability of monomers, (iii)

1. Introduction

1.1. Superacid Catalyzed Polyhydroxyalkylation

Hydroxyalkylation is a Friedel–Crafts aromatic electrophilic substitution reaction. It consists of the condensation of compounds containing the carbonyl group (ketones and aldehydes) with aromatic rings, in the presence of acids, as shown in Figure 1.

The concept of superelectrophilic activation proposed by Olah in the 1970's^[1] to explain the high reactivities of electrophilic species in superacidic media opened a new field in chemistry. Olah and Klumpp^[2] used superacids in hydroxyalkylation

high conversion yields, (iv) high regioselectivities, (v) acceptable reaction times, (vi) great versatility in polymer architectures, (vii) functional groups that allow polymer chemical modification reactions, (viii) easy polymer purification, (ix) good physical, chemical, and thermal properties of the produced polymers, and (x) high polymer molecular weights.

1.2. $A_2 + B_2$ Step-Growth Polymerization

In $A_2 + B_2$ step-growth polymerization, two bifunctional monomers with different functional groups react with one another. Polymers such as the symplest polyamide (Nylon 6/6) and the most commonly available polyester (poly(ethylene terephthalate), (PET)) fall within this polymerization category. For $A_2 + B_2$ polymerization, specifying the chain length n is insufficient because the number of A_2 groups (i) and B_2 groups (j) may differ, giving different end groups. Indeed, as shown in Table 1, there are three types of molecules containing i A_2 groups:^[10,11] “A,” “B,” and “M.”

Polymer molecules type A and B have functional groups A and B as end groups, respectively, whereas polymer molecules type M have an A functional group in one end and a B functional group in the other end of the molecule.

Polymer molecules are represented by P_{ij} , where i represents the number of A_2 groups and j the number of B_2 groups.

J. E. Romero-Hernández, Prof. E. Vivaldo-Lima
Facultad de Química
Departamento de Ingeniería Química
Universidad Nacional Autónoma de México
04510 Ciudad de México, México
E-mail: vivaldo@unam.mx

Dr. A. Cruz-Rosado, Prof. M. G. Zolotukhin
Instituto de Investigaciones en Materiales
Universidad Nacional Autónoma de México
04510 Ciudad de México, México

The ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/mats.201700031>.

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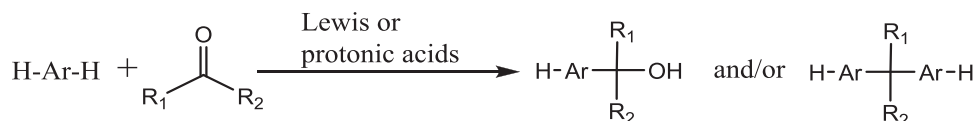


Figure 1. Hydroxyalkylation reaction.

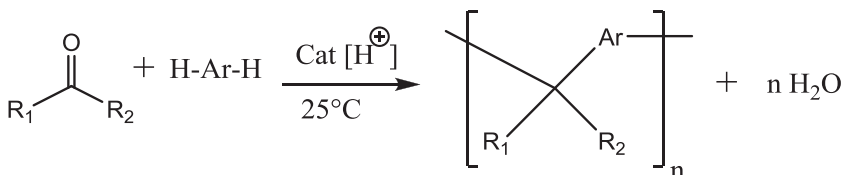


Figure 2. Superacid catalyzed polyhydroxyalkylation.

Monomers A_2 and B_2 are considered polymer molecules of size one and types “A” ($P_{1,0}$) and “B” ($P_{0,1}$), respectively.

Since nonstoichiometric conditions are possible in $A_2 + B_2$ step-growth polymerization, an imbalance stoichiometric ratio, defined by Equation (1), is required.^[10,11] In Equation (1), functional group A is the limiting reagent (B is in excess)

$$r = \frac{[A_2]_0}{[B_2]_0} \leq 1 \quad (1)$$

Four reactions, Equations (2)–(5), are possible in step-growth polymerization. In conventional $A_2 + B_2$ step-growth polymerization, these four reactions occur at the same reaction rate, namely, a single kinetic rate constant, k , is used in the four reactions



Within this framework, the classical theory of $A_2 + B_2$ step-growth polymerization is based on four assumptions:^[7,11] (a) functional groups A and B react at the same rate, irrespective of molecule type (A, B or M), (b) k is independent of chain length (diffusion-controlled effects are absent or negligible); (c) there is no cyclization; and (d) chain length (molecular weight) decreases as the stoichiometric imbalance ratio, r , decreases, which means that the maximum chain length (molecular weight) is reached when $r = 1$.

Table 1. Types of molecules present in $A_2 + B_2$ step-growth polymerization.^[11]

Type of molecule	End groups	Structural formula	Polymer	Constraint
“A”	A–A	(AA – BB) _{i–1} – AA	$P_{i,i–1}$	$i \geq 1$
“B”	B–B	BB – (AA – BB) _i	$P_{i,i+1}$	$i \geq 0$
“M”	A–B	(AA – BB) _{i–1} – AA – BB	$P_{i,i}$	$i \geq 1$

Although it has been proposed that superacid catalyzed polyhydroxyalkylations deviate significantly from the classical behavior of $A_2 + B_2$ step-growth polymerizations,^[3–9] there are no kinetic modeling studies, focused on molecular weight development, reported for this system, which can explain such deviations. It is our objective in this contribution to propose a kinetic model for superacid catalyzed polyhydroxyalkylations focused on molecular weight development.

2. Modeling

2.1. Polymerization Scheme

The polymerization scheme of a conventional $A_2 + B_2$ step-growth polymerization is given by Equations (2)–(5). According to this polymerization scheme, when one of the functional groups is in excess, chain length and, in consequence, molecular weight will decrease. This is explained by the fact that the number of polymer molecules that end in the functional group in excess, in both extremes, will increase. Since the reaction proceeds between A and B only (A does not react with itself and the same occurs with B), this will result in a reduction of molecular weight. However, in superacid catalyzed polyhydroxyalkylations the experimental evidence shows that increasing the excess of one of the functional groups (isatin), which is equivalent to decreasing r in Equation (1), will result in an increase in molecular weight.^[3–9] In order to account for this observation, in this work we assumed that the four reactions of the polymerization scheme shown in Equations (2)–(5) react at different rates, namely, instead of having a single kinetic rate constants, k , we have four: k_{ab} , k_{am} , k_{bm} , and k_{mm} . Subscripts in the kinetic rate constants allude to the polymer molecule types (“A,” “B,” and “M”). The modified polymerization scheme is shown in **Figure 3** for the specific case of isatin and biphenyl, and in **Table 2** for a general case.

Regarding the values of the kinetic rate constants of Table 2 for the systems considered in this contribution, the following assumptions were made, considering the observations made by Zolotukhin and co-workers:^[3–9] (i) kinetic rate constant k_{bm} should be very small ($k_{bm} = 1 \times 10^{-7}$), considering that the carbonyl group from a type B molecule must be protonated prior to its reaction with a type M molecule, and high and positive protonation energies of the electronically deficient carbonyl group contribute to the high activation energy of the first step, thus favoring low k_{bm} values;^[7] (ii) type M molecules react at the same or faster rate with type A molecules than with type B molecules ($k_{am} \geq k_{bm}$); (iii) polymer molecules type A and B react faster with each other than two type M polymer molecules ($k_{ab} > k_{mm}$). It was found for the systems considered in

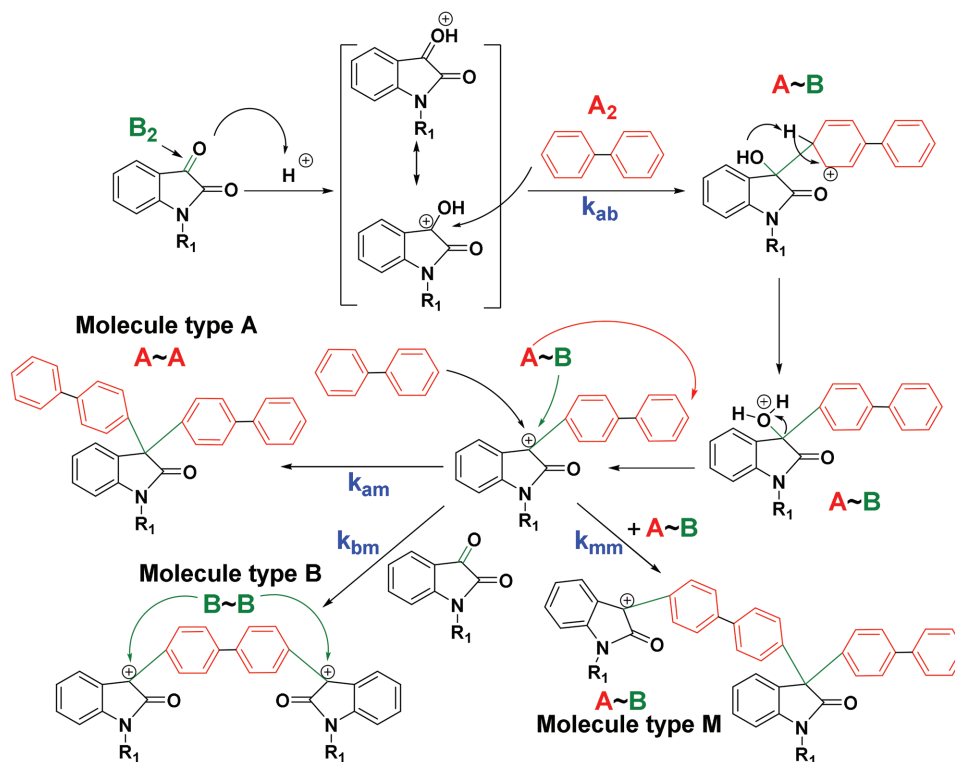


Figure 3. Polymerization scheme for superacid catalyzed polyhydroxyalkylation of isatin and biphenyl. A_2 corresponds to biphenyl monomer and B_2 to the carbonyl functional group.

this study that in general, $k_{bm} \leq k_{am} < k_{mm} < k_{ab}$. With the above conditions the reaction between A and B, to produce type M molecules, proceeds fast. These M molecules react with other M molecules at a slower rate, thus allowing a fast increase in M_n , with a moderate increase in \bar{D} . Eventually, type M molecules will react with A molecules, producing type A molecules. Since the reaction between molecules types M and B will be the slowest one, an excess in B_2 (A_2 is the limiting reagent) will not result in a decrease in M_n ; on the contrary, it will result in ultra-high molecular weights (nonstoichiometric effect).

2.2. Model Equations

Based on the polymerization scheme of Table 2, Equations (6)–(8) can be derived. If all the reactions proceeded at the same rate,

Table 2. Polymerization scheme for superacid catalyzed polyhydroxyalkylations.

Reaction	Step
Molecule type "A" with "B"	$A \sim A + B \sim B \xrightarrow{k_{ab}} A \sim B$
Molecule type "A" with "M"	$A \sim A + A \sim B \xrightarrow{k_{am}} A \sim A$
Molecule type "B" with "M"	$B \sim B + A \sim B \xrightarrow{k_{bm}} B \sim B$
Molecule type "M" with "M"	$A \sim B + A \sim B \xrightarrow{k_{mm}} A \sim B$

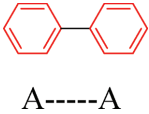
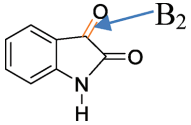
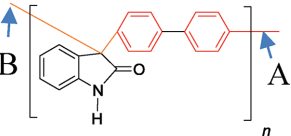
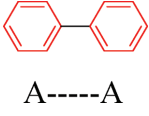
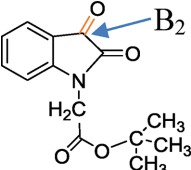
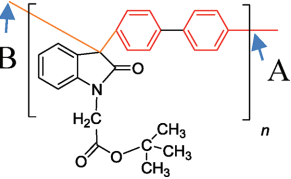
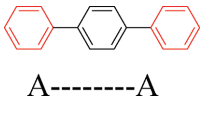
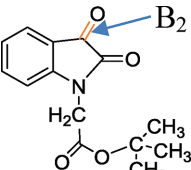
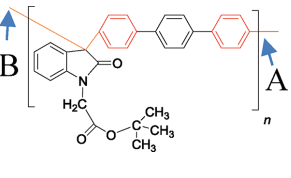
namely, if $k_{bm} = k_{am} = k_{mm} = k_{ab}$, these equations would be the same as those obtained by Gordon and Temple^[10] and Dotson et al.^[11] for a conventional $A_2 + B_2$ step-growth polymerization. To simplify notation, single index variables for A, B, and M polymer molecules will be used. We introduced variables A_i , B_i , and C_i , defined by Equations (9)–(11). The moments of these polymer populations are defined in Table 3. Applying the method of moments to Equations (6)–(8), Equations (12)–(14) are obtained. Number and weight average molecular weights, M_n and M_w , are calculated from Equations (15) and (16), respectively. Molar mass dispersity, \bar{D} , is calculated using Equation (17).

Table 3. Definition of moment equations for the polymer distribution of superacid catalyzed polyhydroxyalkylation.

Species	Definition of moment ^{a)}
Polymer type A	$\alpha_m = \sum_{i=1}^{\infty} i^m A_i$
Polymer type B	$\beta_m = \sum_{i=1}^{\infty} i^m B_i$
Polymer type M	$\mu_m = \sum_{i=1}^{\infty} i^m C_i$

^{a)}Note on subscripts: $m = 0, 1, 2, \dots$

Table 4. Description of studied systems in superacid-catalyzed polymerization.

System	Monomer A ₂	Monomer B ₂	Polymer type M	Catalyst/co-catalyst
(a) Isatin + biphenyl				TFSA
(b) Modified isatin + biphenyl				TFSA/TFA
(c) Modified isatin + terphenyl				TFSA/TFA

As explained in Section 1, cyclization was neglected in our polymerization scheme. This is a reasonable assumption since the use of superacids and nonstoichiometric conditions promotes the formation of polymer molecules with the same functional group in both chain ends, thus reducing cyclization efficiency, since there is no cyclization between identical functional groups^[5]

Mass balance equation for molecules type “A”

$$\frac{dP_{i,i-1}}{dt} = 2k_{am} \sum_{s=1}^{i-1} P_{s,s-1} P_{i-s,i-s} - 2P_{i,i-1} \left\{ 2k_{ab} \sum_{s=0}^{\infty} P_{s,s+1} + k_{am} \sum_{s=1}^{\infty} P_{s,s} \right\} \quad (6)$$

Table 5. Adjusted kinetic parameters for superacid catalyzed polyhydroxyalquilation of isatin and modified isatin with biphenyl and terphenyl.

Reaction system	Parameter, units	Value
(a) Isatin + biphenyl	k_{ab} , dm ³ mol ⁻¹ s ⁻¹	8.43905×10^{-3}
	k_{am} , dm ³ mol ⁻¹ s ⁻¹	8.43905×10^{-5}
	k_{bm} , dm ³ mol ⁻¹ s ⁻¹	1×10^{-7}
	k_{mm} , dm ³ mol ⁻¹ s ⁻¹	8.35466×10^{-4}
(b) Modified isatin + biphenyl	k_{ab} , dm ³ mol ⁻¹ s ⁻¹	5.7×10^{-3}
	k_{am} , dm ³ mol ⁻¹ s ⁻¹	1×10^{-7}
	k_{bm} , dm ³ mol ⁻¹ s ⁻¹	1×10^{-7}
	k_{mm} , dm ³ mol ⁻¹ s ⁻¹	5×10^{-3}
(c) Modified isatin + terphenyl	k_{ab} , dm ³ mol ⁻¹ s ⁻¹	9.1×10^{-4}
	k_{am} , dm ³ mol ⁻¹ s ⁻¹	9×10^{-4}
	k_{bm} , dm ³ mol ⁻¹ s ⁻¹	1×10^{-7}
	k_{mm} , dm ³ mol ⁻¹ s ⁻¹	4.1×10^{-4}

Table 6. Adjusted parameters for DC-effects in superacid catalyzed polyhydroxyalquilation of modified isatin with biphenyl and terphenyl.

Reaction system	Parameter	r	a _i	b _i , s ⁻¹
(b) Modified isatin + biphenyl	k_{ab}	1	0.15	0.8875
	k_{am}	1	0.15	0.8875
	k_{bm}	1	0.15	0.8875
	k_{mm}	1	0.25	0.8875
	k_{ab}	10/11	0.575	1.2
	k_{am}	10/11	0.575	1.2
	k_{bm}	10/11	0.575	1.2
	k_{mm}	10/11	0.675	1.2
	k_{ab}	10/12	0.1	0.7705
	k_{am}	10/12	0.1	0.7705
	k_{bm}	10/12	0.1	0.7705
	k_{mm}	10/12	0.28	0.7705
(c) Modified isatin + terphenyl	k_{ab}	1	0.425	0.365
	k_{am}	1	0.425	0.365
	k_{bm}	1	0.425	0.365
	k_{mm}	1	0.7	0.365
	k_{ab}	10/11	0.475	0.585
	k_{am}	10/11	0.475	0.585
	k_{bm}	10/11	0.475	0.585
	k_{mm}	10/11	0.985	0.585
	k_{ab}	10/12	0.252	0.3215
	k_{am}	10/12	0.252	0.3215
	k_{bm}	10/12	0.252	0.3215
	k_{mm}	10/12	0.652	0.3215
k_{ab}	10/13	0.1	0.085	
k_{am}	10/13	0.1	0.085	
k_{bm}	10/13	0.1	0.085	
k_{mm}	10/13	0.3	0.085	

Table 7. Initial conditions for superacid catalyzed polyhydroxalquiliations.

Reaction system	Property, units	Value	Comments
(a) Isatin + biphenyl	$[A_2]_0, \text{mol L}^{-1}$	0.15	Initial concentration of monomer A_2
	r	$1, \frac{10}{11}, \frac{10}{11.5}, \frac{10}{13}, \frac{10}{17}, \frac{10}{20}$	Stoichiometric imbalance ratio
	$PM_0, \text{g mol}^{-1}$	$\frac{297}{2}$	Molecular weight of repetitive unit
(b) Modified isatin + biphenyl	$[A_2]_0, \text{mol L}^{-1}$	0.15	Initial concentration of monomer A_2
	r	$1, \frac{10}{11}, \frac{10}{12}$	Stoichiometric imbalance ratio
	$PM_0, \text{g mol}^{-1}$	$\frac{409}{2}$	Molecular weight of repetitive unit
(c) Modified isatin + terphenyl	$[A_2]_0, \text{mol L}^{-1}$	0.35	Initial concentration of monomer A_2
	r	$1, \frac{10}{11}, \frac{10}{12}, \frac{10}{13}$	Stoichiometric imbalance ratio
	$PM_0, \text{g mol}^{-1}$	$\frac{473}{2}$	Molecular weight of repetitive unit

Mass balance equation for molecules type “B”

$$\frac{dP_{i-1,i}}{dt} = 2k_{\text{bm}} \sum_{s=0}^{i-1} P_{s,s+1} P_{i-s,i-s} - 2P_{i-1,i} \left\{ 2k_{\text{ab}} \sum_{s=1}^{\infty} P_{s,s-1} + k_{\text{bm}} \sum_{s=1}^{\infty} P_{s,s} \right\} \quad (7)$$

Mass balance equation for molecules type “M”

$$\frac{dP_{i,i}}{dt} = 4k_{\text{ab}} \sum_{s=0}^{i-1} P_{s,s+1} P_{i-s,i-s-1} + 2k_{\text{mm}} \sum_{s=1}^{i-1} P_{s,s} P_{i-s,i-s} - 2P_{i,i} \left\{ k_{\text{bm}} \sum_{s=0}^{\infty} P_{s,s+1} + k_{\text{am}} \sum_{s=1}^{\infty} P_{s,s-1} + k_{\text{mm}} \sum_{s=1}^{\infty} P_{s,s} \right\} \quad (8)$$

Change of variable for molecules type “A”

$$A_i = P_{i,i-1} \quad (9)$$

Change of variable for molecules type “B”

$$B_i = P_{i-1,i} \quad (10)$$

Change of variable for molecules type “M”

$$C_i = P_{i,i} \quad (11)$$

Moment equations for molecules type “A”

$$\frac{d\alpha_m}{dt} = 2k_{\text{am}} \sum_{s=0}^m \binom{m}{s} \alpha_s \mu_{m-s} - 2\alpha_m \{ 2k_{\text{ab}} \beta_0 + k_{\text{am}} \mu_0 \} \quad (12)$$

Moment equations for molecules type “B”

$$\frac{d\beta_m}{dt} = 2k_{\text{bm}} \sum_{s=0}^m \binom{m}{s} \beta_s \mu_{m-s} - 2\beta_m \{ 2k_{\text{ab}} \alpha_0 + k_{\text{bm}} \mu_0 \} \quad (13)$$

Moment equations for molecules type “M”

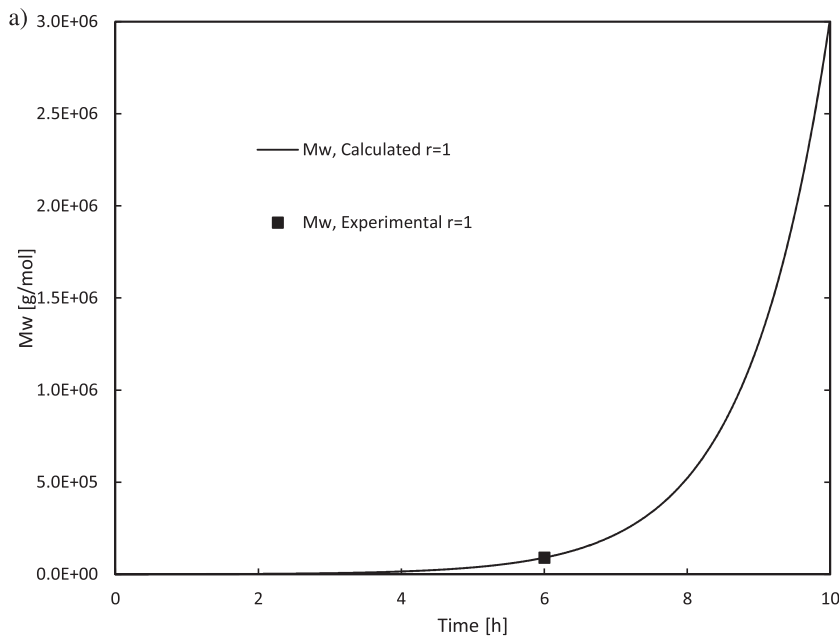
$$\frac{d\mu_m}{dt} = 4k_{\text{ab}} \sum_{s=0}^m \binom{m}{s} \beta_s \alpha_{m-s} + 2k_{\text{mm}} \sum_{s=0}^m \binom{m}{s} \mu_s \mu_{m-s} - 2\mu_m \{ k_{\text{am}} \alpha_0 + k_{\text{bm}} \beta_0 + k_{\text{mm}} \mu_0 \} \quad (14)$$

$$\bar{M}_n = \left[\frac{\alpha_1 + \beta_1 + \mu_1}{\alpha_0 + \beta_0 + \mu_0} \right] \cdot PM_0 \quad (15)$$

$$\bar{M}_w = \left[\frac{\alpha_2 + \beta_2 + \mu_2}{\alpha_1 + \beta_1 + \mu_1} \right] \cdot PM_0 \quad (16)$$

$$\mathfrak{D} = \frac{\bar{M}_w}{\bar{M}_n} \quad (17)$$

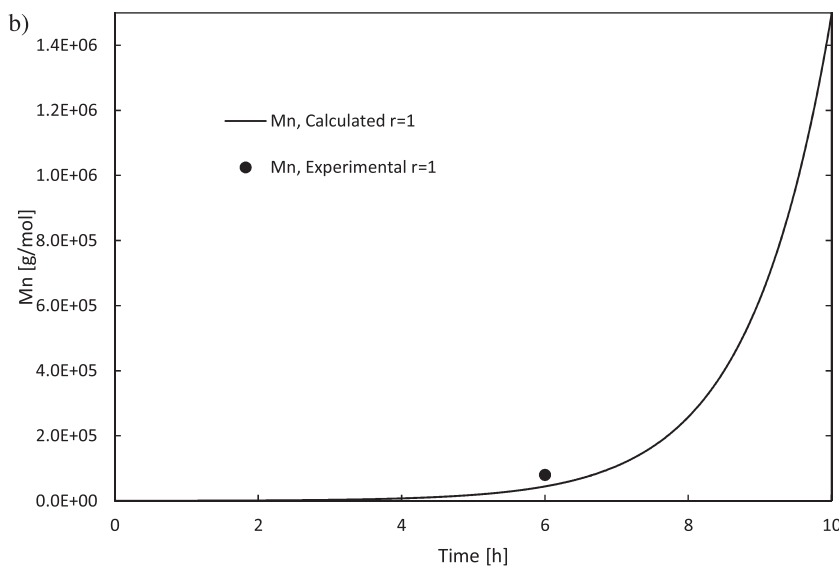
Since ultrahigh molecular weights are obtained in superacid catalyzed polyhydroxalquiliations, it is likely that diffusion-controlled (DC) effects can become important at medium to high conversions. Free-volume theory,^[12–15] Equation (18), was used in our model to account for DC-effects. k in Equation (18) is effective kinetic rate constant, k_0 is intrinsic kinetic rate constant, V_{f0} is fractional free volume at initial conditions, V_f is fractional free volume at time t , and β is a free-volume parameter. Fractional free-volume is calculated using Equation (19), where T is reaction temperature, T_{gi} is glass transition temperature for component i , V_i is volume for component i , and V_t is total volume. Since we did not have enough information about free-volume parameters for our monomers, we rewrote Equation (18) as Equation (20), where a_i and b_i are free volume parameters for component i , defined by Equations (21) and (22), respectively



$$\frac{\beta_i}{v_i} = b_i \frac{t}{3600} \quad (22)$$

2.3. Kinetic and Free-Volume Parameters

As shown in Table 4, three polymerization systems were considered in this study: (a) polymerization of isatin and biphenyl, (b) polymerization of modified isatin and biphenyl, and (c) polymerization of modified isatin and terphenyl. The kinetic parameters used in this study are summarized in Table 5. Systems (b) and (c) (polymerizations of modified isatin with biphenyl and terphenyl, respectively) required to take into account DC-effects, as explained in the preceding section. The parameters associated to DC-effects used for systems (b) and (c) are summarized in Table 6.



2.4. Numerical Issues

The model consists of nine ordinary differential equations: Equations (12)–(14) with $m = 0, 1$, and 2, namely, three moment equations for each polymer type (A, B, and M). The equations were solved using Rosenbrock's method in the Maple mathematical software.

3. Results and Discussion

3.1. Systems Studied

As explained in Section 2.3, three systems were addressed in this contribution. The initial reaction conditions of the three systems studied are summarized in Table 7. The experimental data used for parameter estimation and model validation purposes were obtained from Zolotukhin and co-workers.^[3–9] Although specific details on the measurement of molecular weight distributions by gel permeation chromatography-multiple angle laser light scattering (GPC-MALLS) for the systems considered in this study are provided in the cited references, [3–9] it is worth mentioning here that several solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), and tetrahydrofuran (THF), were tested for polymer solubility. Solvent selection criteria for the GPC-MALLS equipment considered reproducibility and correlation with independent measurements of inherent viscosity obtained with an Ubbelohde viscometer. DMF was used in the case of the polymers studied here.^[6] A bank of two Styragel columns, HR 4E, and HR 5E (dimensions 7.8 mm × 300 mm), both with a mixed-bed pore size (50 to 1.0 × 10⁶ Å), and particle size 3 and 5 μm was used.

Figure 4. Comparison of model predictions and experimental data of: a) M_w versus time, and b) M_n versus time, for the superacid catalyzed polyhydroxyalkylation of isatin with biphenyl ($r = 1$).

$$k = k_0 \exp \left[-\beta \left(\frac{1}{V_f} - \frac{1}{V_{f0}} \right) \right] \quad (18)$$

$$V_f = \sum_{i=1}^N \left[0.025 + \alpha_i (T - T_{gi}) \right] \frac{V_i}{V_i} \quad (19)$$

$$k_i = k_i^0 \exp \left[a_i - b_i \frac{t}{3600} \right] \quad (20)$$

$$a_i = \frac{\beta_i}{v_i^2} \quad (21)$$

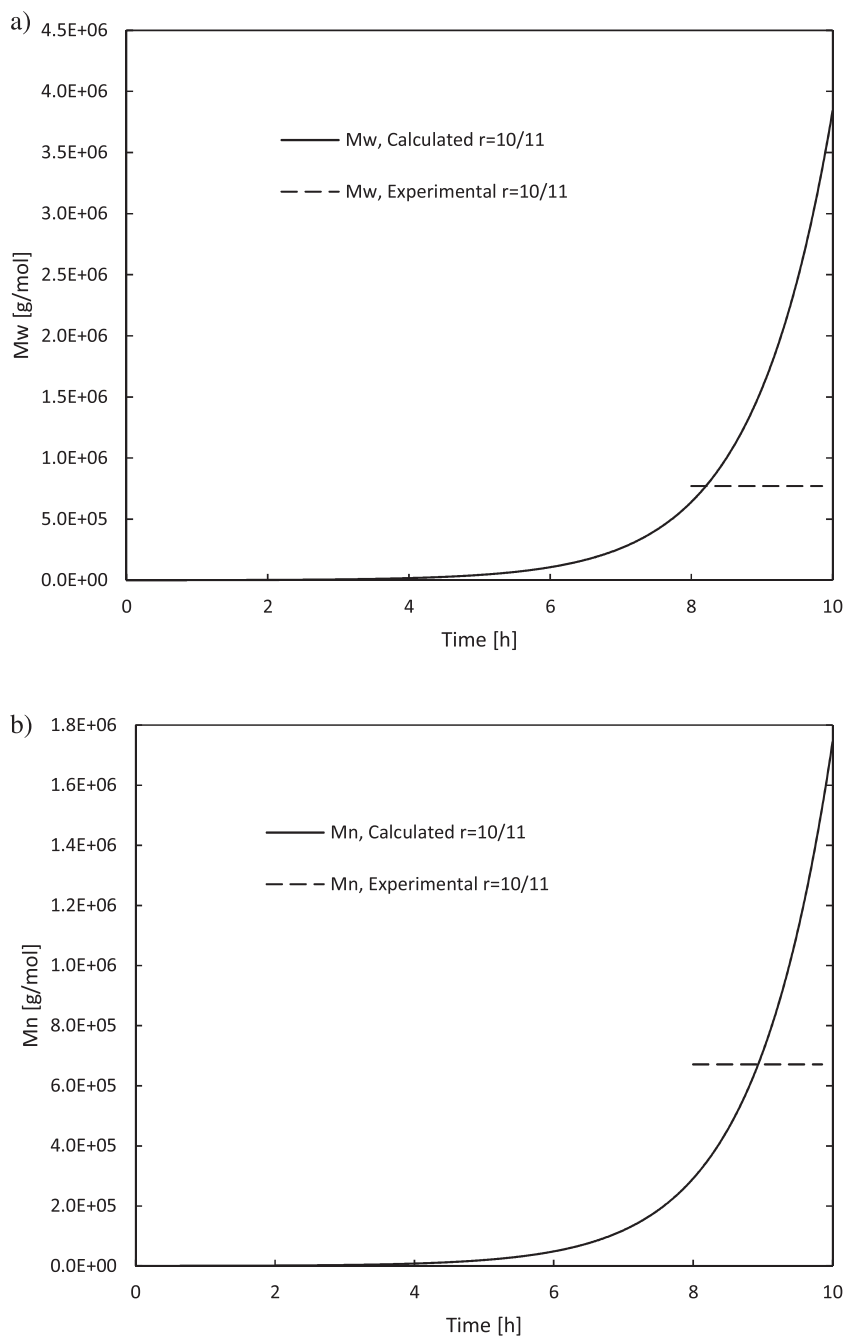


Figure 5. Comparison of model predictions and experimental data of: a) M_w versus time, and b) M_n versus time, for the superacid catalyzed polyhydroxyalkylation of isatin with biphenyl ($r = 10/11$).

The temperature of the columns was controlled at 50 °C by the thermostat.^[6] Our strategy consisted of choosing a subset of the available experimental data for parameter estimation purposes and the remaining experimental data were used to test the predictive power of the model by simulating conditions outside the experimental region used for parameter estimation purposes (interpolation and extrapolation simulations).

Initially, there were only monomers A_2 and B_2 present in the reaction system. Therefore, there were no type M molecules

present in the system at the beginning of the polymerization. This means that at $t = 0$, α_0 , α_1 , and $\alpha_2 = [A_2]_0$, β_0 , β_1 , $\beta_2 = [B_2]_0$, and μ_0 , μ_1 , $\mu_2 = 0$.

3.2. Comparison of Model Predictions against Experimental Data

For system (a) (isatin and biphenyl), the experimental data used for parameter estimation purposes were the ones at stoichiometric conditions ($r = 1$); for system (b) (modified isatin and biphenyl) the subset used was that corresponding to $r = 10/12$; experimental data at $r = 10/13$ were used for parameter estimation purposes in system (c) (modified isatin and terphenyl).

The experimental data that we used for parameter estimation purposes were the measurements of M_w by GPC-MALLS, since in principle that technique provides absolute values of M_w .

3.2.1. Analysis of the Isatin and Biphenyl Reaction System

Figure 4–9 show molecular weight development (M_n , M_w and \bar{D} versus time) for superacid catalyzed polyhydroxyalkylation of isatin with biphenyl at different stoichiometric imbalance ratios (different r values). In this case, DC-effects were neglected. Since no kinetic studies were originally planned in the early stages of this research line, only one data point at each condition was available. However, having experimental data at several stoichiometric imbalance ratios and with several monomers provides enough information as to assess the adequacy and performance of our model. In some cases (when $r < 1$), the exact time at which the polymerization was stopped was not available. In those cases a dashed line covering the possible sampling time interval was used instead of a single data point. Good agreement between calculated and experimental values of M_w and M_n is observed in all the cases analyzed. It is also observed that

molecular weight increases as r decreases, which coincides with the observed experimental trend for these systems.^[3–9] Although M_w keeps increasing as r decreases, an optimal value of $r = 10/11.5$ (0.87) at which M_n is maximum, is observed.

In spite of the fact that our predictions of M_n and M_w versus time agree well with experimental data, when one plots them as dispersity (\bar{D}) versus time, as in **Figure 7c**, a significant deviation is observed (the measured values by MALLS are much lower than the calculated ones). Similar results are obtained for the

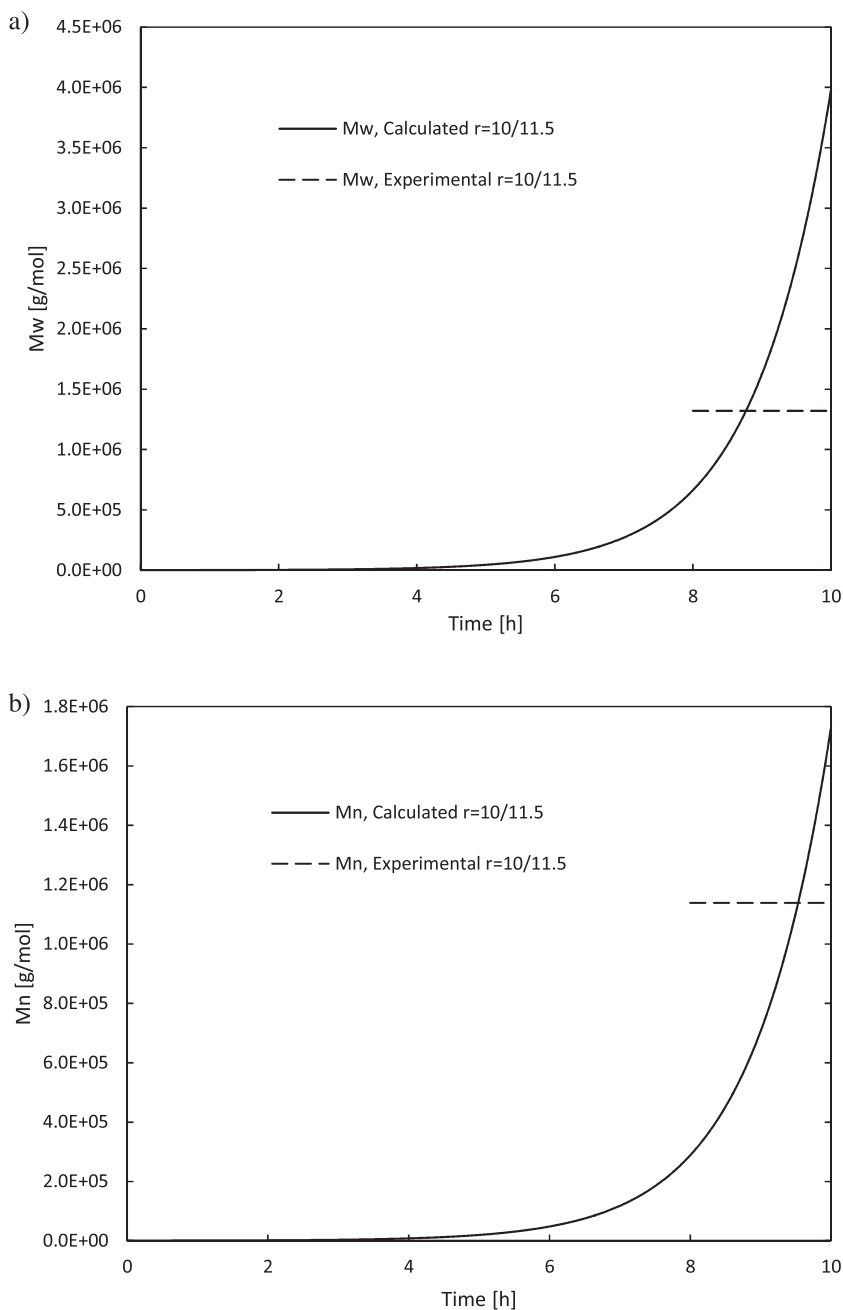


Figure 6. Comparison of model predictions and experimental data of: a) M_w versus time, and b) M_n versus time, for the superacid catalyzed polyhydroxyalkylation of isatin with biphenyl ($r = 10/11.5$).

other cases using these monomers, but we decided to include only one of such plots. Although our M_w values are supposed to be reliable since they came from MALLS measurements,^[3–9] a technique which in principle provides absolute values, it has been observed that unrealistically low \bar{D} values can be obtained in situations such as the synthesis of water soluble polymers by free-radical polymerization (FRP) (preliminary measurements prior to actual reported results),^[16–19] or the copolymerization of limonene with acrylic monomers by FRP (preliminary measurements prior to actual reported results),^[20–24] if the MALLS

detector is not properly aligned (assure correct peak alignment), or if dn/dc is not calculated from actual polymer concentrations. In some cases, the best configuration for a MALLS detector was using only the 90° detector, plus angular correction.^[16–19] Also, it is documented in the literature that the MALLS technique is limited to 10–30 nm in radius of gyration (r_g), which corresponds to $\approx 100\,000$ to 500 000 Da for linear polystyrene.^[25] For $r_g > 30$ nm it is necessary to know the actual conformation of the polymer molecules to get accurate values of r_g .^[25] Wyatt^[26] questioned these limits which were based on calculations from data obtained with “faulty columns and questionable separations achieved,” and criticized some theoretical aspects related to data analysis, pointing out that precision can be improved by making more measurements, measuring a sample at a higher concentration if concentration effects are negligible, and using a shorter wavelength light source. Wyatt^[26] also cited an unpublished symposium report that broadens these limits of M_w to 30 000–9 000 000 Da for linear polystyrene samples, using MALLS detectors. So, M_w data obtained from MALLS detectors require implementing and following nontrivial operational and data analysis procedures which, if not properly followed, may end up in not fully reliable M_w measurements for ultrahigh molecular weight polymers.

An important aspect to point out is that in cases where the measured results of \bar{D} using MALLS detectors violate theoretical restrictions, such as $\bar{D} < 1.5$ (conventional FRP (the theoretical restriction is $\bar{D} \geq 1.5$), the user can detect that a problem or error occurred and take proper actions, as was done in the cases of the synthesis of water soluble polymers by FRP^[16–19] and the copolymerization of limonene with acrylic monomers by FRP^[20–24] as mentioned above. In the case of ideal $A_2 + B_2$ step-growth polymerization, the theoretical dispersity range is $1 \leq \bar{D} \leq 2$. So, obtaining $\bar{D} \approx 1.5$ for ultrahigh molecular weight polymers synthesized by superacid catalyzed polyhydroxyalkylations^[3–9] was surprising but not necessarily suspicious. Future experimental studies from our group will pay special attention to this issue in order to determine if the disagreement between calculated and experimental \bar{D} values is caused by alignment issues with the MALLS detector, or by model inadequacy.

3.2.2. Analysis of the Modified Isatin and Biphenyl Reaction System

Figure 10 shows plots of M_w (Figure 10a), M_n (Figure 10b), and \bar{D} (Figure 10c) versus time for the superacid catalyzed

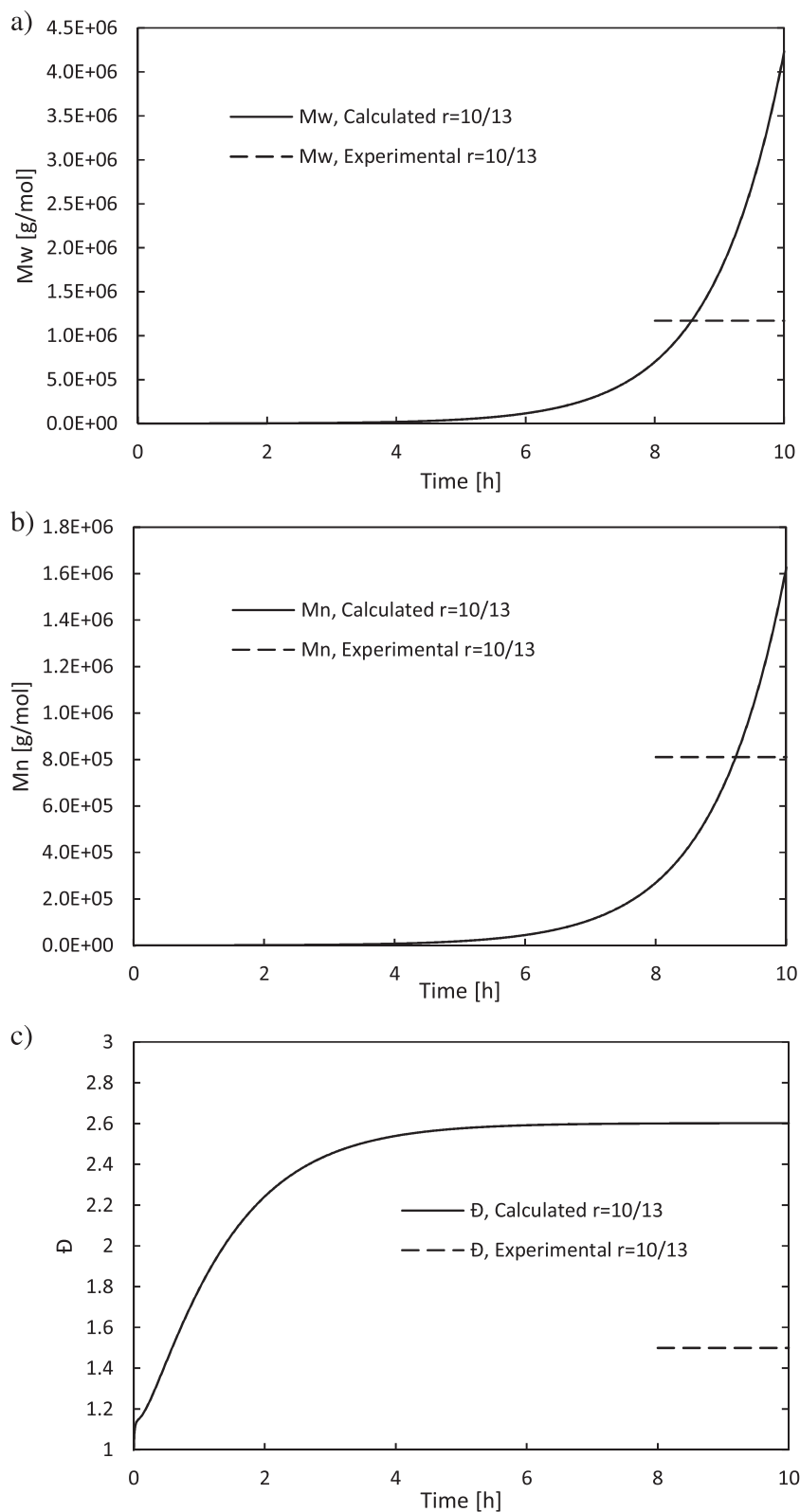


Figure 7. Comparison of model predictions and experimental data of: a) M_w versus time, b) M_n versus time, and, c) \bar{D} versus time, for the superacid catalyzed polyhydroxyalkylation of isatin with biphenyl ($r = 10/13$).

polyhydroxyalkylation of modified isatin with biphenyl at $r = 10/11$, which was the case used for parameter estimation purposes. Although the model without DC-effects predicts very high final molecular weights, another phenomenon seems to be acting during the polymerization, affecting molecular weight development (evolution in time of M_w), since the agreement with experimental data is poor. One possibility is that DC-effects (reduction of mobility of polymer molecules as viscosity increases) can play a role at high molecular weights and high polymer concentrations.^[12–15] It was difficult to assess if DC-effects are important in the case of polyhydroxyalkylation of isatin and biphenyl (case analyzed in Section 3.2.1), since only molecular weight experimental data was available at final polymerization conditions (a single data point per value of r studied). Figure 10a confirms that inclusion of DC-effects improves the agreement between model predictions and experimental data of M_w versus time when modified isatin is used. However, the agreement of experimental data and model predictions for M_n (see Figure 10b) and, in consequence \bar{D} (Figure 10c), is not as good as with M_w .

Figure 11 shows plots of M_w , M_n , and \bar{D} versus time for the superacid catalyzed polyhydroxyalkylation of modified isatin with biphenyl at different stoichiometric imbalance ratios, including the case mentioned above for parameter estimation purposes ($r = 10/11$). DC-effects were included in all the cases shown in Figure 11. As observed in Figure 11a, the model predicts the observed experimental trend of increasing M_w as r is decreased, and the agreement between calculated profiles and experimental data is very good for $r = 1$ and $r = 10/11$. The same trend but less good agreement with experimental data is observed in Figure 11b for M_n . However, the first three data points of molecular weight at $r = 10/12$ clearly deviate from the observed trend. Interestingly, the agreement between calculated and experimental data for the \bar{D} versus time profile is better in this case than the previous one using isatin. Still, the experimental \bar{D} values are lower than the calculated ones.

The disagreement between calculated and experimental profiles of \bar{D} versus time may be associated to inaccurate measurements of M_w with the MALLS detector, as explained in the previous subsection. However, another aspect that may contribute

to the disagreement between experimental data and calculated profiles, particularly for M_w and M_n versus time when $r = 10/12$, is the fact that the chemical modification of isatin (insertion of tert-butyl acetate at the isatin groups along the polymer chain) took place with a polymer from isatin and biphenyl, and not with isatin monomer itself. That is, we are

approximating the insertion of tert-butyl acetate, at the isatin position, to a polymer produced from superacid catalyzed polyhydroxyalkylation of isatin and biphenyl, with the superacid catalyzed polyhydroxyalkylation of modified isatin (a monomer already containing the tert-butyl acetate molecule within the structure of isatin) and biphenyl.

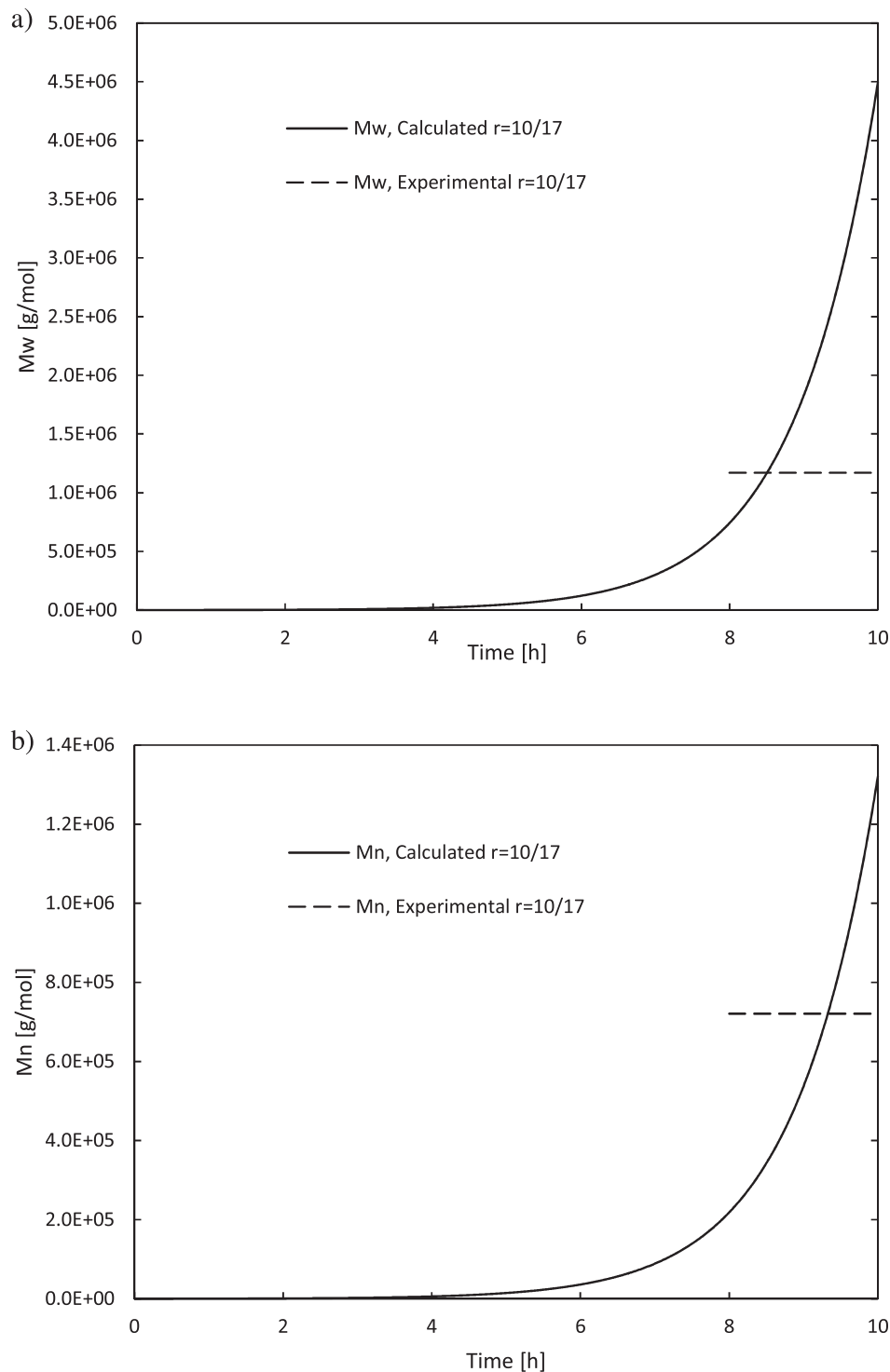


Figure 8. Comparison of model predictions and experimental data of: a) M_w versus time, and b) M_n versus time, for the superacid catalyzed polyhydroxyalkylation of isatin with biphenyl ($r = 10/17$).

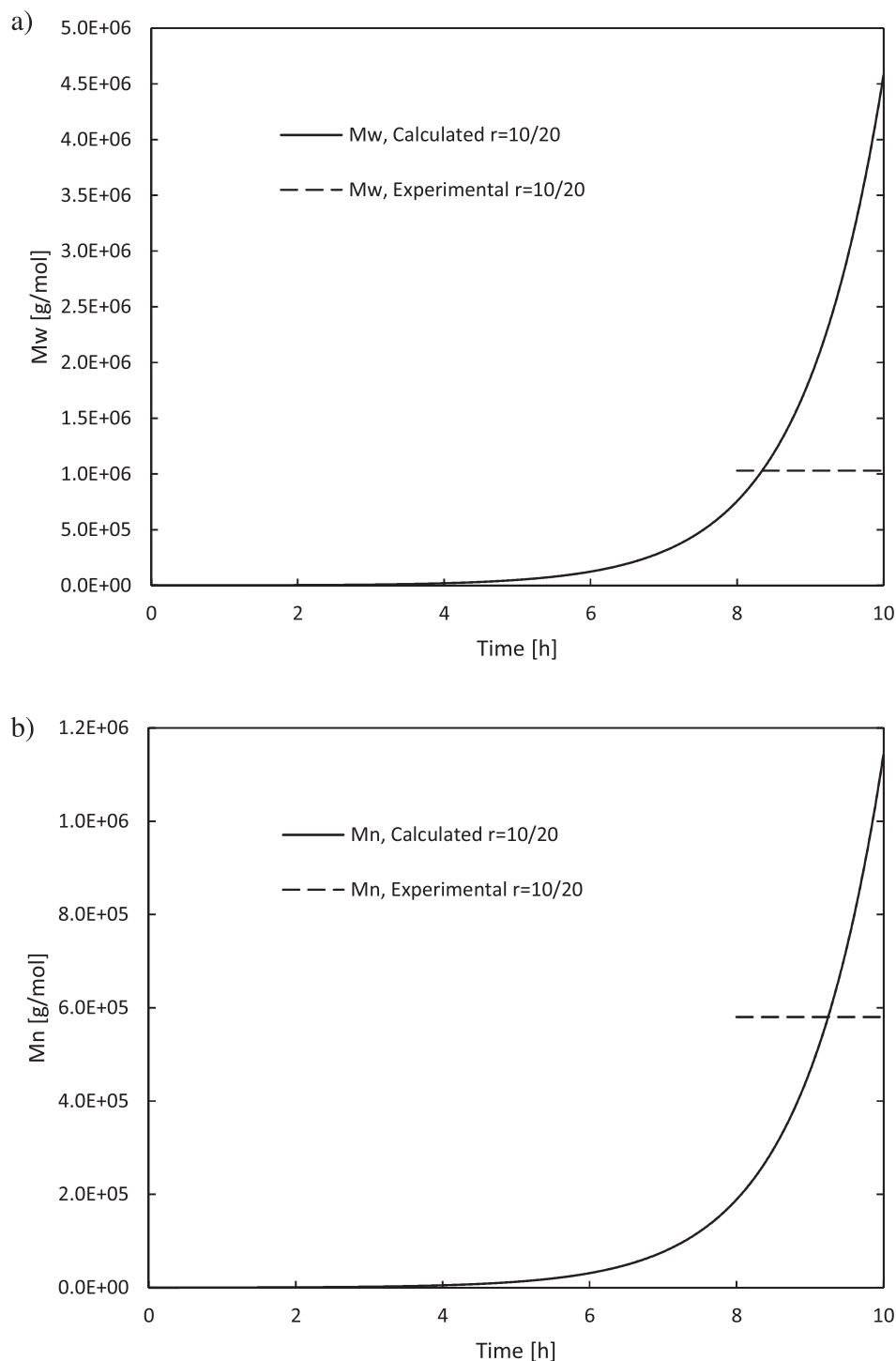


Figure 9. Comparison of model predictions and experimental data of: a) M_w versus time, and, b) M_n versus time, for the superacid catalyzed polyhydroxyalkylation of isatin with biphenyl ($r = 10/20$).

3.2.3. Analysis of the Modified Isatin and Terphenyl Reaction System

The last reaction system considered in this paper is the superacid catalyzed polyhydroxyalkylation of modified isatin with terphenyl. As in the case of superacid catalyzed polyhydroxyalkylation

of modified isatin and biphenyl, in this case our model was an approximation, since the actual system was the insertion of tert-butyl acetate, at the isatin position, to a polymer produced from superacid catalyzed polyhydroxyalkylation of isatin and terphenyl.

Figure 12 shows plots of M_w (Figure 12a), M_n (Figure 12b), and \bar{D} (Figure 12c) versus time for the superacid catalyzed

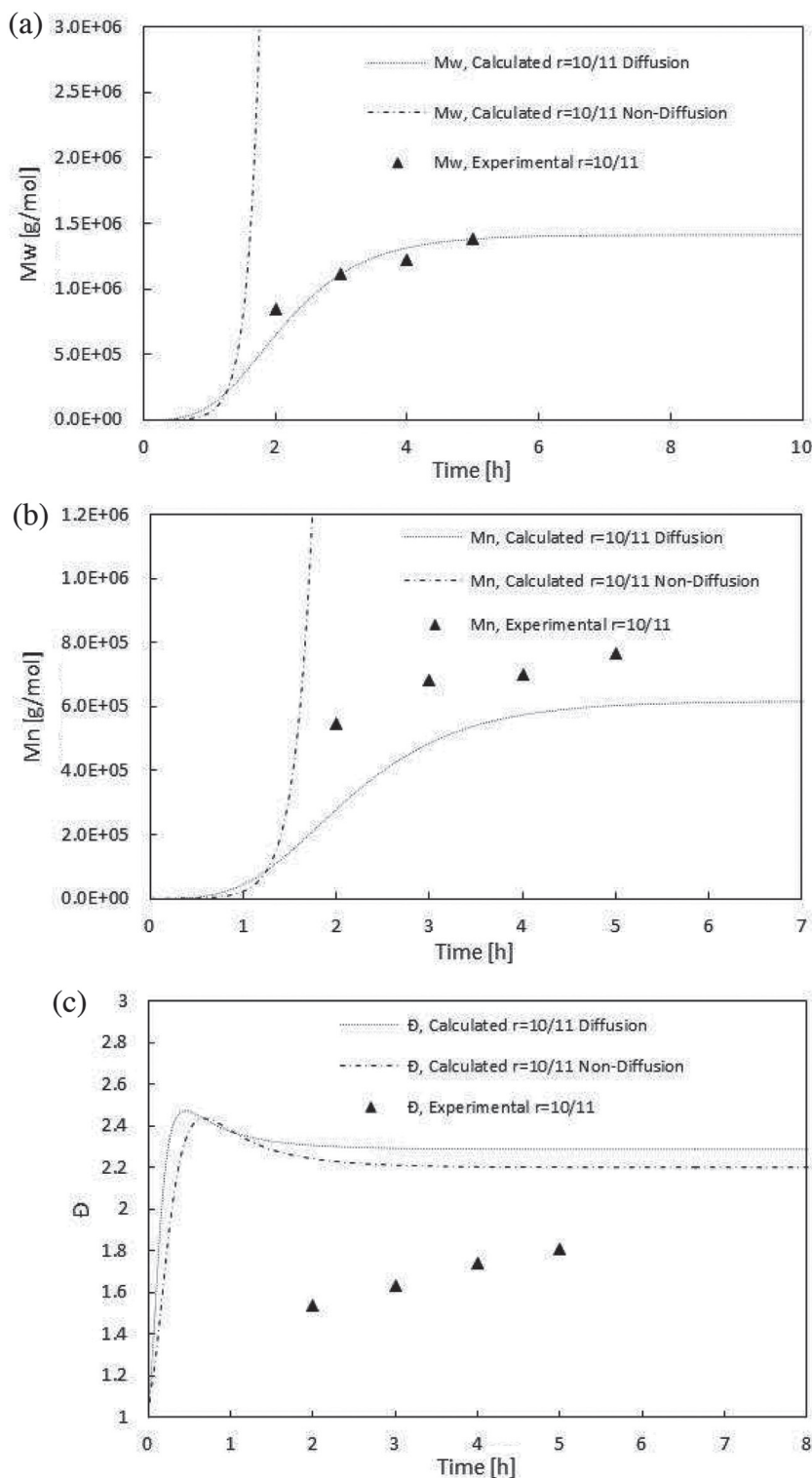


Figure 10. Comparison of model predictions and experimental data of: a) M_w versus time, b) M_n versus time, and c) \bar{D} versus time, for the superacid catalyzed polyhydroxyalkylation of modified isatin and biphenyl at $r = 10/11$. Calculated profiles with and without DC-effects.

polyhydroxyalkylation of modified isatin with terphenyl at $r = 10/13$, which was the case used for parameter estimation purposes. Although qualitatively, the incorporation of DC-effects

with terphenyl. Our model for cases (b) and (c) was an approximation since those polymerizations actually consisted of superacid catalyzed polyhydroxyalkylation of isatin with biphenyl or

in this system follows the expected trend of reducing molecular weight as time elapses (see Figure 12a,b). In this case both profiles (with and without DC-effects) fit equally well the experimental data, since the model differences occur after 7.5 h, where there are no experimental data available. The agreement between calculated and experimental profiles of M_w and M_n versus time is fairly good. Once again, the calculated profile of \bar{D} versus time is significantly higher than the experimental data. This mismatch may be related to the likely inaccurate measurements of M_w with the MALLS detector, as discussed earlier for the other two systems.

Figure 13 shows plots of M_w , M_n , and \bar{D} versus time for the superacid catalyzed polyhydroxyalkylation of modified isatin and terphenyl at different stoichiometric imbalance ratios, excluding the case used for parameter estimation purposes ($r = 10/13$), which is shown in Figure 12 and not repeated in Figure 13 due to scale difference issues. DC-effects were included in all the cases shown in Figure 13. The experimental trends are well captured by the model, but the agreement between calculated profiles and experimental data of M_w , M_n , and \bar{D} versus time, although better than the previous case with biphenyl, is not very good.

4. Conclusion

The superacid catalyzed polyhydroxyalkylation of isatin and modified isatin with biphenyl and terphenyl was modeled as an $A_2 + B_2$ step-growth polymerization with different kinetic rate constants for each one of the four reactions involved in the polymerization scheme. It was thus demonstrated that the apparent violation of the classical theory of $A_2 + B_2$ step-growth polymerization by production of ultrahigh molecular weight polymer at imbalance stoichiometric ratios smaller than one is just a result of proving the theory at conditions not previously considered. Still, this is the first modeling approach considering molecular weight development for this fairly new polymerization system.

Three polymerization systems were considered: (a) superacid catalyzed polyhydroxyalkylation of isatin and biphenyl, (b) superacid catalyzed polyhydroxyalkylation of modified isatin with biphenyl, and (c) superacid catalyzed polyhydroxyalkylation of modified isatin

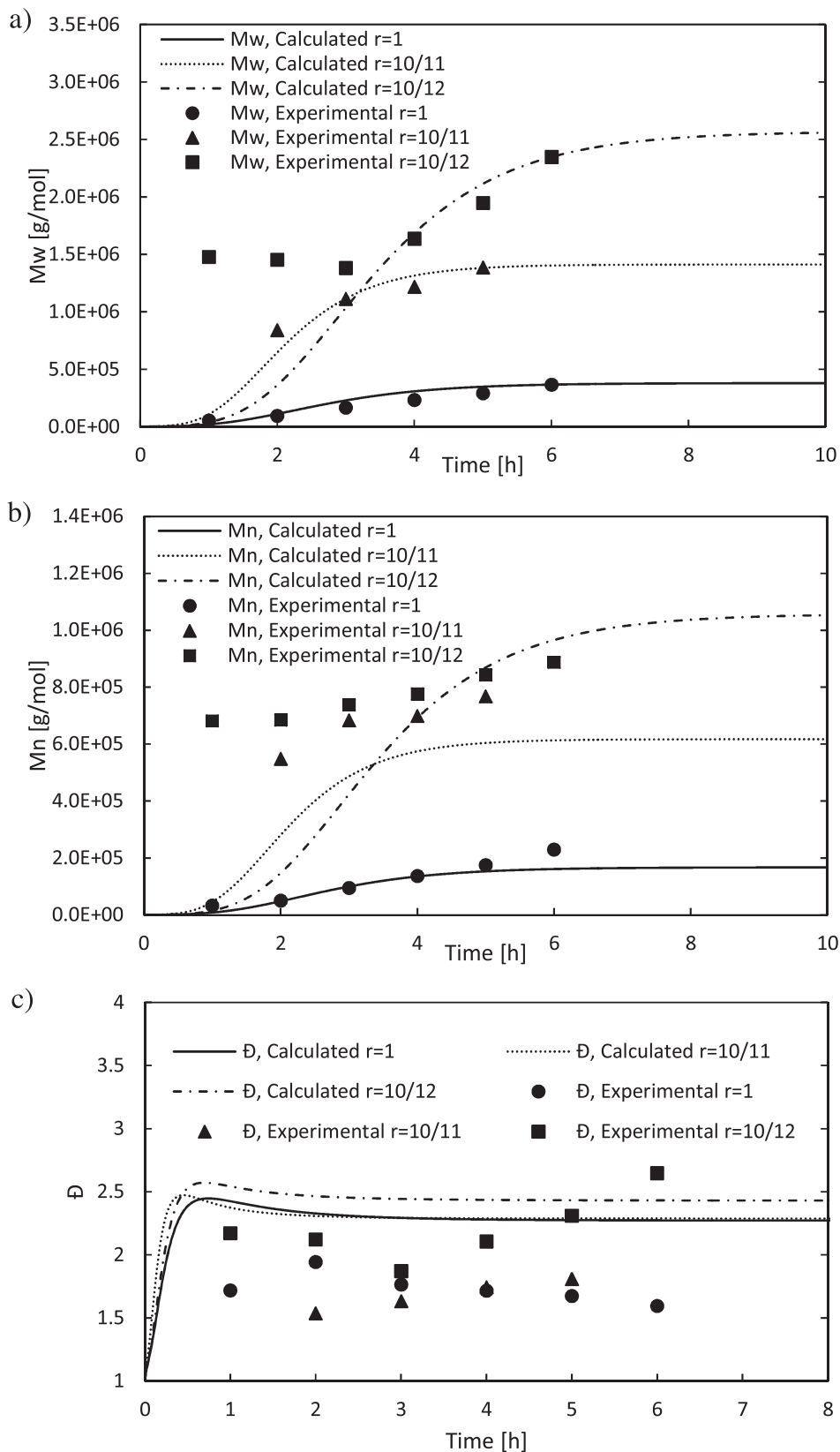


Figure 11. Comparison of model predictions (including DC-effects) and experimental data of: a) M_w versus time, b) M_n versus time, and, c) \bar{D} versus time, for the superacid catalyzed polyhydroxyalkylation of modified isatin with biphenyl.

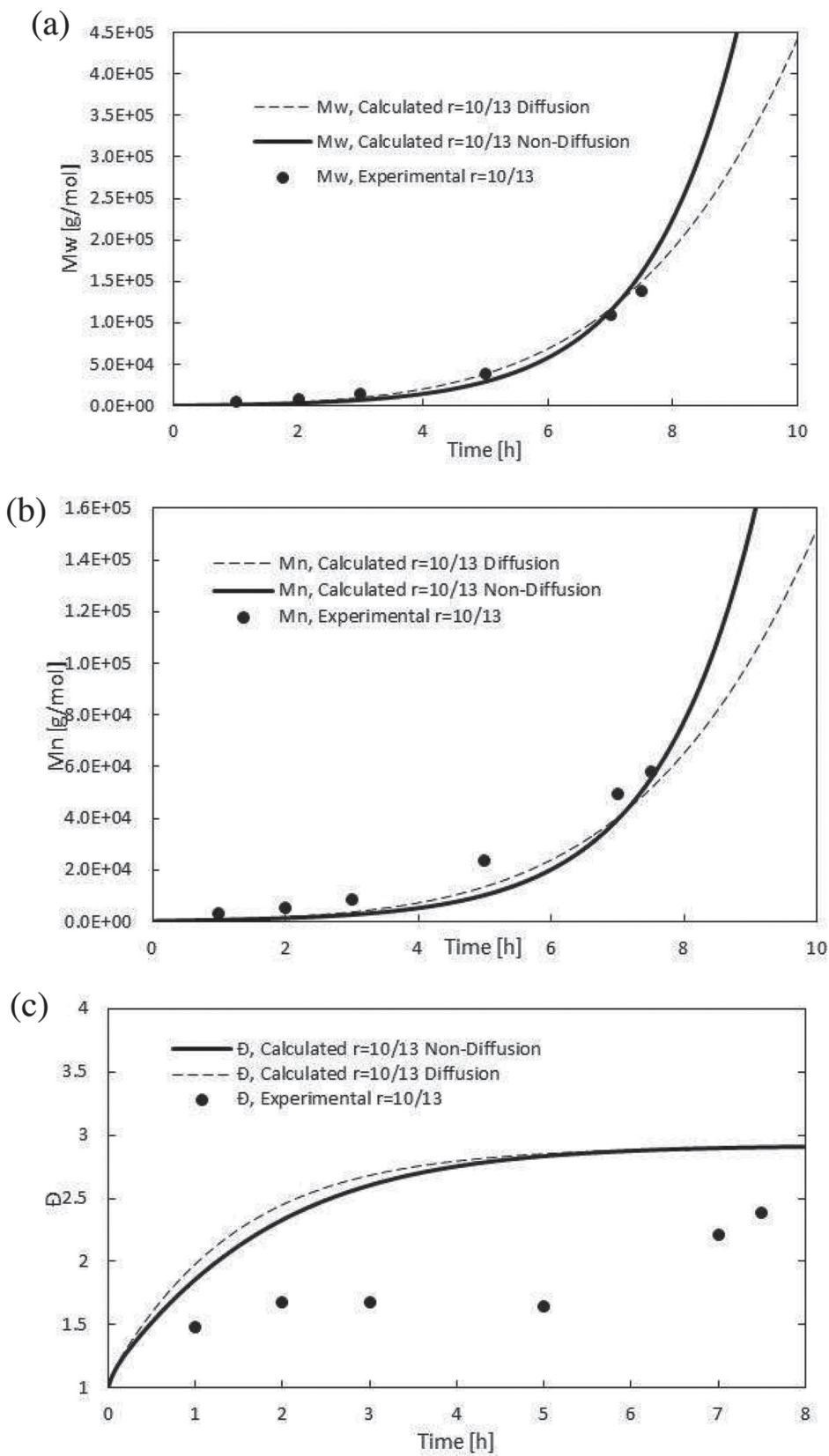


Figure 12. Comparison of model predictions and experimental data of: a) M_w versus time, b) M_n versus time, and c) \bar{D} versus time for the superacid catalyzed polyhydroxyalkylation of modified isatin and terphenyl at $r = 10/13$.

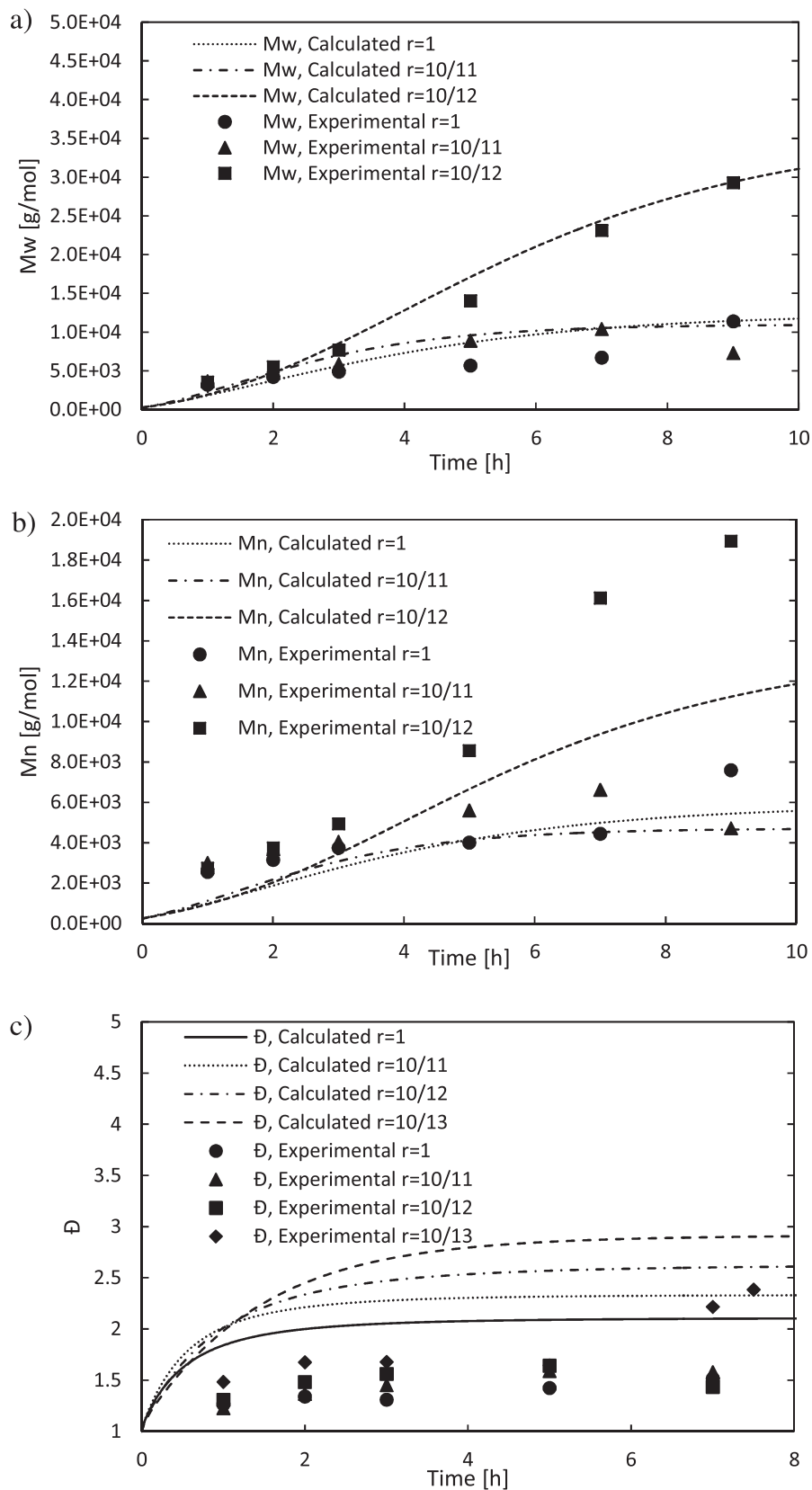


Figure 13. Comparison of model predictions and experimental data of: a) M_w versus time, b) M_n versus time, and, c) \bar{D} versus time, for the superacid catalyzed polyhydroxyalkylation of modified isatin with terphenyl at different r values.



terphenyl followed by chemical modification (insertion of tert-butyl acetate at the isatin groups along the polymer chain) of the produced polymer. The agreement between calculated and experimental profiles of M_w , M_n , and \mathcal{D} versus time was from fairly to very good. DC-effects were considered for cases (b) and (c) but were important only for case (b). In case (c), the experimental data available had been obtained at conversion levels where DC-effects are still unimportant. The unusually low dispersities observed experimentally in the three cases (predicted values were significantly higher) may be related to inaccurate measurement of M_w by GPC using a MALLS detector. The disagreement between experimental and calculated profiles of M_w and M_n versus time, particularly for case $r = 10/12$, may be related to the fact that the modification of isatin was carried out in polymer molecules produced using isatin monomer and not modified isatin monomer. However, it is also possible that our model is neglecting important phenomena that may be important for molecular weight development.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

$A_2 + B_2$ step-growth polymerization, bi- and terphenyl, isatin, mathematical modeling, nonstoichiometric step-growth polymerization, polymerization kinetics, superacid catalyzed polyhydroxyalkylations

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