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ORIGINAL ARTICLE

Synthesis of “bioinspired” copolymers: experimental and theoretical investigation on poly(vinyl benzyl thymine-co-triethyl ammonium chloride)

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“Bioinspired” copolymers based on vinylbenzyl thymine (VBT) and an ionically-charged monomer, such as vinylbenzyl triethylammonium chloride (VBA), were synthesized and theoretically investigated. These water-soluble copolymers are polystyrene- (PS) based, and their structure mimics DNA. In the presence of short-wavelength UV light, the thymine groups dimerize into non-toxic, environmentally benign, and biodegradable photo-resistant materials. Copolymerizations with different comonomer ratios were carried out at 65°C. Samples were taken along the reactions to determine monomer conversion, chemical composition, and molecular weight distribution. While average molecular weights fall along the reaction, the average composition remains almost constant and coincident with the initial comonomer ratios, thus indicating a similar reactivity of all the comonomer radicals. A mathematical model was developed that simulates the synthesis of the base biopolymer, in the sense of predicting the evolution of the global reaction variables and molecular structure of the polymer. The termination and propagation kinetic constants were adjusted to the experimental data. The resulting values are quite different to those of a normal styrene homopolymerization, thus suggesting a noticeable effect of the solvent and the comonomer pending groups.

Keywords: Biopolymer; thymine polymer; crosslinking; biomimicry

Nomenclature

A	VBT comonomer
$A_{m,n}^{\bullet}$	A-ended macroradical with m repeating units of A and n repeating units of B
B	VBA comonomer
$B_{m,n}^{\bullet}$	B-ended macroradical with m repeating units of A and n repeating units of B
$C_{m,n}$	Dead copolymer species with m repeating units of A and n repeating units of B
f	Efficiency factor of the chemical initiator
I_2	Chemical initiator
\bar{M}_n	Number-average molecular weight of the copolymer
m_P	Mass of polymer contained in a sample
m_S	Sample mass
\bar{M}_w	Weight-average molecular weight of the copolymer
R_c^{\bullet}	Primary initiator radical
t	Time
T	Temperature
V	Volume
w_{Sv}^0	Weight fraction of solvent in the reaction recipe
x	Conversion

Introduction

The increasing attention directed to the environmental and toxicological implications associated with commercial materials, together with the high energy inputs required for most existing processes, suggest that environmentally-benign alternatives must be explored (1). A smart way to do this is to mimic “mother nature” (2). In this context, the synthetic monomer (4-vinyl benzyl) thymine (VBT) was investigated (3–16,20). It is especially interesting for its ability to photo-crosslink upon irradiation of short UV wavelength (~ 280 nm), which is present in sunlight (17,18).

“Bioinspired” polymers containing thymine are similar to polystyrene (PS), except that thymine and charged functional groups are chemically bonded onto the base PS structure. The chemistry of crosslinking and immobilization of these bioinspired polymers has been derived from a simple photochemical transformation that occurs in nature: the $2\pi + 2\pi$

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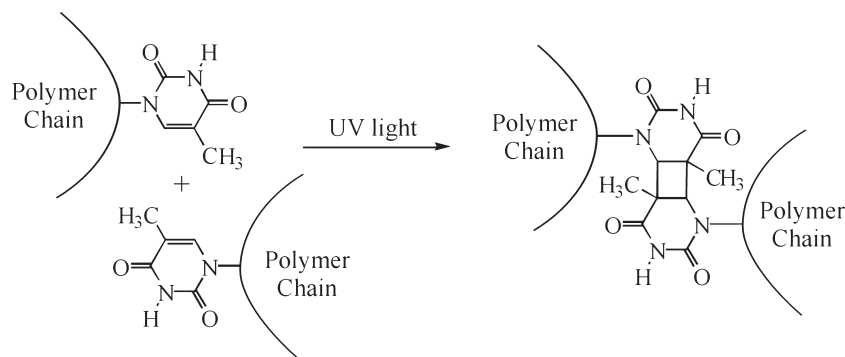


Figure 1. Photoinduced dimerization of thymine containing polymers. Adapted from Ref. (12).

photo-dimerization of thymine base units within DNA when exposed to UV radiation (Figure 1) (17,18).

To produce water-soluble polymers, VBT can be copolymerized in a free-radical process with ionically-charged comonomers, such as vinyl benzyl triethyl ammonium chloride (VBA), yielding (random and cationic) linear copolymers of controlled composition (Figure 2).

The adaptability of VBT makes it an attractive monomer, since the balance between photoreactivity, solubility, and non-covalent interactions can be fine-tuned for a wide variety of applications. In addition, the existence of natural mechanisms to reverse the photo-dimerization reaction and to restore the polymers to their original state provides exciting opportunities to create fully recyclable materials (14). Some practical applications involve hair-styling products (11), electrically conductive coatings (13), antibacterial-coated surfaces (12), controlled-release drug-delivery systems (16,19), recyclable plastics (10,14), and photo-resists (5–8,15) including fabrication of electronic components and printed circuit boards. Besides the large variety of potential applications, these thymine-based PS are environmentally-benign and consistent with the Twelve Principles of Green Chemistry (1): a non-toxic, water-soluble, and

biodegradable material, which requires low energies for processing (20).

The molecular structure (molecular weight distribution and chemical composition) and the physical properties (solubility and photoreactivity) of the thymine containing polymers are determined by the synthesis conditions (i.e. molar ratio between the comonomers, type of comonomers, monomer-to-solvent ratio, reaction temperature, residence time, reaction system, etc.). These characteristics together with the conditions of the curing process determine the final (thermal and mechanical) properties of the polymer. The inter-relationships between the synthesis conditions, biopolymer structure, curing conditions, and final mechanical and thermal properties are a challenging issue that is, at present, only beginning to be understood.

In this work, VBT-VBA copolymers are synthesized and theoretically investigated, with the aim of determining the molecular structure of the copolymer.

Mathematical modeling and simulation results

A mathematical model was developed for the copolymerization of VBT and VBA. It is based on the global kinetic mechanism presented in Table 1. The comonomer structures are similar to the structure of styrene

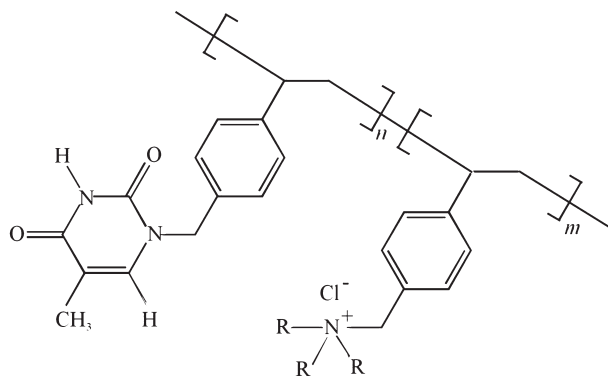


Figure 2. Water-soluble copolymer of (VBT) $_n$ -(VBA) $_m$.

Table 1. Kinetic mechanism ($m, n, r, q = 0, 1, 2, \dots, \infty$).

Initiation	
$I_2 \xrightarrow{k_d} 2R_c^\bullet$	
$R_c^\bullet + A \xrightarrow{k_{iA}} A_{1,0}^\bullet$	
$R_c^\bullet + B \xrightarrow{k_{iB}} B_{0,1}^\bullet$	
Propagation	
$A_{m,n}^\bullet + A \xrightarrow{k_{pAA}} A_{m+1,n}^\bullet$	
$B_{m,n}^\bullet + B \xrightarrow{k_{pBB}} B_{m,n+1}^\bullet$	
$A_{m,n}^\bullet + B \xrightarrow{k_{pAB}} B_{m,n+1}^\bullet$	
$B_{m,n}^\bullet + A \xrightarrow{k_{pBA}} A_{m+1,n}^\bullet$	
Chain transfer to the monomers	
$A_{m,n}^\bullet + A \xrightarrow{k_{tAA}} C_{m,n} + A_{1,0}^\bullet$	
$B_{m,n}^\bullet + B \xrightarrow{k_{tBB}} C_{m,n} + B_{0,1}^\bullet$	
$A_{m,n}^\bullet + B \xrightarrow{k_{tAB}} C_{m,n} + B_{0,1}^\bullet$	
$B_{m,n}^\bullet + A \xrightarrow{k_{tBA}} C_{m,n} + A_{1,0}^\bullet$	
Termination by recombination	
$A_{m-r,n-q}^\bullet + A_{r,q}^\bullet \xrightarrow{k_{tAA}} C_{m,n}$	
$B_{m-r,n-q}^\bullet + B_{r,q}^\bullet \xrightarrow{k_{tBB}} C_{m,n}$	
$A_{m-r,n-q}^\bullet + B_{r,q}^\bullet \xrightarrow{k_{tAB}} C_{m,n}$	

(St); and for this reason the standard (low temperature) kinetics of St was adopted (21), which include chemical initiation, propagation, transfer to the monomer, and termination by recombination. Since reactions were carried out at low temperature, a negligible effect is expected of the transfer to the monomer. The nomenclature is as follows: A and B represents the VBT and VBA comonomers, respectively; I_2 is the chemical initiator; R_c^\bullet is the primary initiator radical; $A_{m,n}^\bullet$, $B_{m,n}^\bullet$ and $C_{m,n}$ are A-ended macroradicals, B-ended macroradicals, and dead polymer chains, respectively, where m is the number of A repeating units and n the number of B repeating units; k_d is the initiator decomposition rate constant; k_{iA} and k_{iB} are the comonomer initiation rate

constants; k_{pAA} , k_{pBB} , k_{pAB} , and k_{pBA} are the propagation rate constants; k_{tAA} , k_{tBB} , k_{tAB} , and k_{tBA} are the constants of chain transfer to the comonomers; and k_{iAA} , k_{iBB} , and k_{iAB} are the rate constants of termination by recombination. The kinetic mechanism assumptions are (a) the radical reactivity only depends on the terminal unit; (b) the reactivity of primary monomer radicals $A_{1,0}^\bullet$ and $B_{0,1}^\bullet$ coincide with those of their corresponding macroradicals $A_{m,n}^\bullet$ and $B_{m,n}^\bullet$, respectively; and (c) the rate constants are independent of the chain length.

The mathematical model is presented in Appendix A. It involves the molar balances of reagents and products in a discontinuous stirred-tank reactor. The main assumptions were (a) homogeneous and isothermal polymerization; (b) long-chain approximation (by which comonomers are only consumed in the propagation reactions); and (c) the gel effect is neglected (acceptable for dilute solution polymerizations). The model inputs are the temperature and the initial masses of reagents. The model outputs are the species concentrations, the global comonomer conversion, and the copolymer molecular structure. The basic module is constituted by Eqs. (A.1)–(A.4) and (A.9)–(A.10) (which calculate the global concentrations), and by Eq. (A.11) (that calculates the monomer conversion). The detailed module is given by Eq. (A.12), which calculates the bivariate number-chain length distribution (NCLD) of the evolving copolymer. Then, the average molecular weights are estimated through Eqs. (A.13)–(A.14).

The system of differential equations (A.1)–(A.4), (A.9)–(A.10), and (A.12) was solved through a (second-order modified) Rosenbrock numerical method. A simplified method that calculates a reduced number of (fictitious) species was applied to Eq. (A.12) (21). The computation time of a typical run was less than 1 min on a Pentium IV IBM-compatible PC.

Table 2 presents the employed kinetic parameters. For comonomer A, the reactivity ratio measures the probability of an A-ended free radical to react with A or with B. Similarly, for comonomer B, the reactivity ratio measures the probability of a B-ended free radical to react with B or with A. Elemental analysis

Table 2. Kinetic parameters.

f (—)	0.68	Ref. (22)
k_d (1/s)	1.507×10^{-5}	Ref. (23)
k_{tAA} , k_{tBB} , k_{tAB} , k_{tBA} , (1/(mol s))	3.017×10^{-2}	Ref. (21)
k_{pAA} , k_{pBB} , k_{pAB} , k_{pBA} , k_p (1/(mol s))	10.144	Adjusted in this work
k_{iAA} , k_{iBB} , k_{iAB} , k_i , (1/(mol s))	1.804×10^3	Adjusted in this work
k_{iA} , k_{iB} , (1/(mol s))	6.450	Ref. (21)

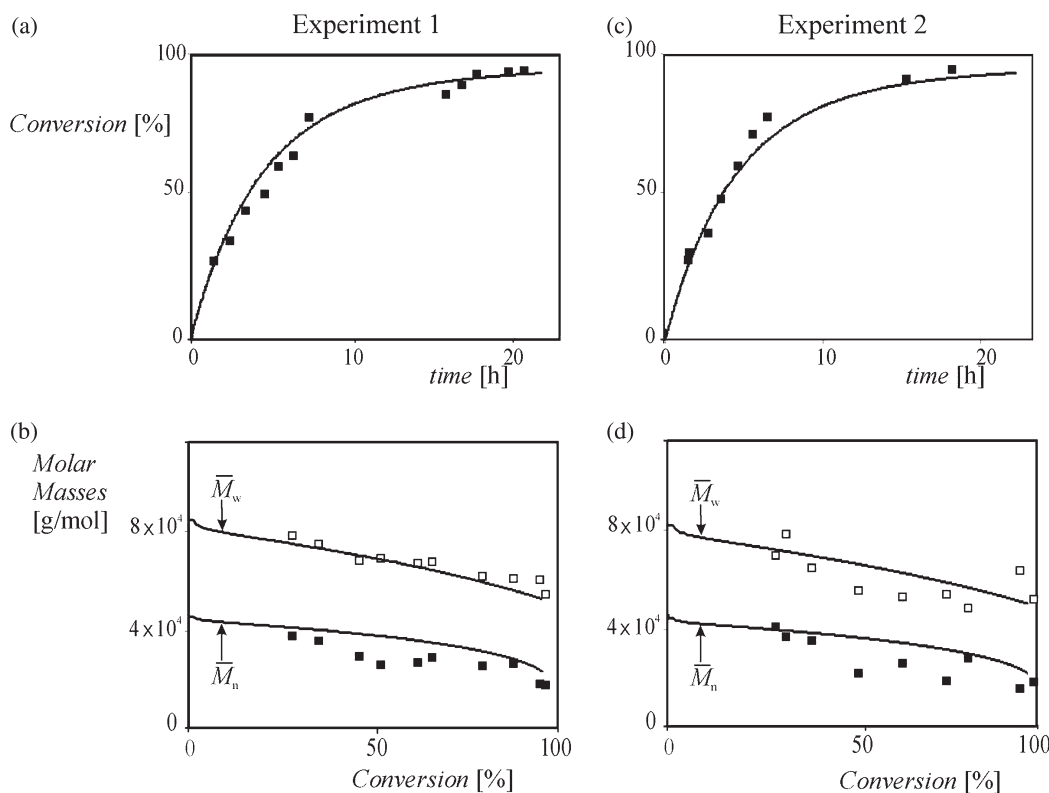


Figure 3. Experiments 1 and 2. (a,c) Time evolution of comonomer conversion. (b,d) Copolymer average molar masses versus conversion. Measurements are in symbols and model predictions are in continuous trace.

results suggest that both reactivity ratios are close to unity, and for this reason the following was adopted: $k_{pAA} = k_{pBB} = k_{pAB} = k_{pBA} = \text{generic } k_p$; $k_{fAA} = k_{fBB} = k_{fAB} = k_{fBA} = \text{generic } k_f$; and $k_{tAA} = k_{tBB} = k_{tAB} = k_{tBA} = \text{generic } k_t$. Under the mentioned assumptions and considering pseudo-steady state for radical species, the following function for polymerization rate (R_p) with the kinetic constants is obtained:

$$R_p = k_p([A] + [B])([A^\bullet] + [B^\bullet])$$

$$= k_p([A] + [B]) \frac{(2fk_d[I_2])^{1/2}}{k_t^{1/2}} \quad (1)$$

While f , k_d , k_{iA} , k_{iB} , and k_f were directly taken from the literature (21–23), the generic k_p and k_t were adjusted through the following two-step procedure: (i) $k_p/k_t^{1/2}$ (Eq. 1) was adjusted to fit the experimental conversions of Figure 3(a,c); and (ii) with the (fixed) $k_p/k_t^{1/2}$ ratio, k_p was adjusted to fit the average molecular weights of Figure 3(b,d). Note that molecular weights are affected by the individual values of k_p and k_t . At low reaction temperatures, transfer reactions are almost negligible (25). The procedure was implemented with a Nelder–Mead technique (24), which minimizes the difference between the measurements and their corresponding model predictions. For the solution, polymerization of St in

benzene at the 60°C, Estenoz et al. (25) reported the following values: $k_p = 160$ l/mol s; and $k_t = 6.41 \times 10^6$ l/mol s. With respect to these values, the adjusted constants k_p and k_t of Table 2 are both considerably lower. These large differences suggest that the reactivities and/or diffusivities of comonomers and radicals are strongly affected by the nature of the solvent and of the (polar and ionic) pending groups in VBT and VBA, respectively.

Figure 3 compares the experimental results with the model predictions, and a reasonable agreement is observed. The reduction of the average molecular weights with conversion is explained in terms of fast comonomers consumption with respect to the initiator consumption (Figure 4). Note that at the end of the reactions (at $t \cong 20$ h), the initiator conversion was about 65%, while the comonomers conversion was almost 100% (Figure 4).

Experimental work

Copolymer synthesis

Several VBT-VBA copolymerizations were carried out at 65°C. Table 3 presents the recipes for Experiments 1 and 2. Unless specifically noted, all the reagents and materials were from Sigma-Aldrich, and were used as

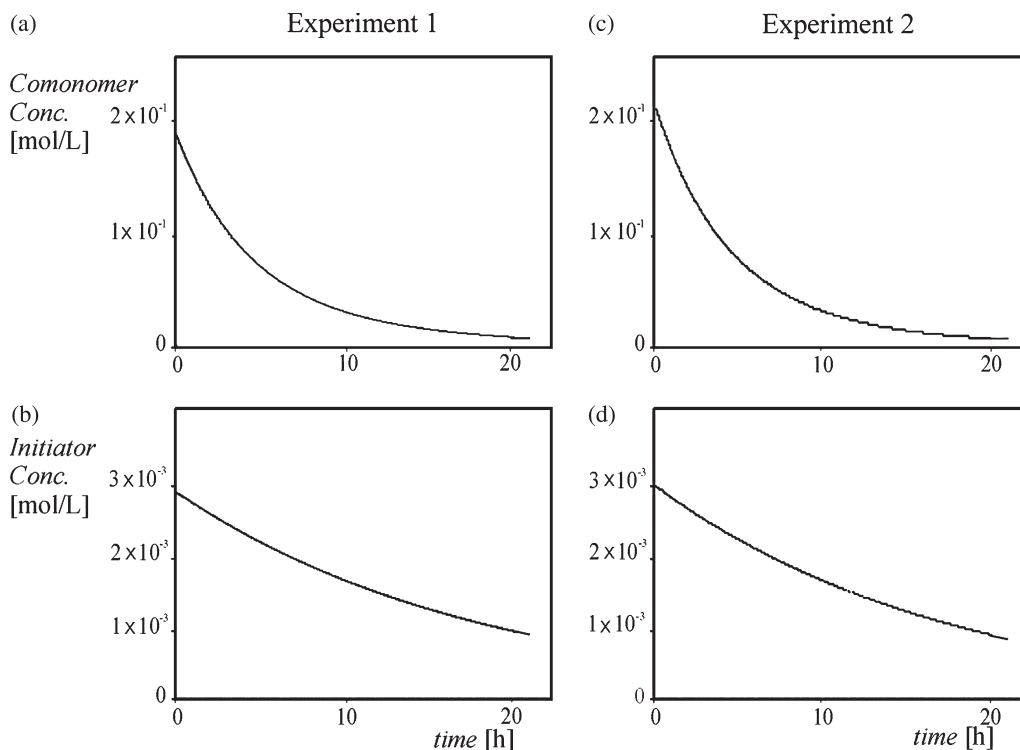


Figure 4. Experiments 1 and 2: model predictions for the time evolutions of the total concentration of unreacted comonomers (a,c); and of the unreacted initiator (b,d).

received. As described in Cheng et al. (4), VBT was synthesized from thymine and vinyl benzyl chloride, while VBA was obtained from vinyl benzyl chloride and triethylamine. Reactions were carried out in a 250-ml glass reactor equipped with an external heating jacket and a turbine-type stirrer. The experiments involved an initial (1 h) dissolution period of the comonomers in isopropanol at room temperature. Then, the mixture was heated from room temperature to 65°C; and the initiator (2,2'-azobisisobutyronitrile; AIBN) was added. Nitrogen gas at a flow rate of 15–20 cm³/min was bubbled through for 20 min before adding the initiator, and throughout the reaction, to eliminate dissolved oxygen. The temperature was manually controlled at 65°C by manipulating the temperature of the heating bath. Reactions were carried out up to almost complete conversion, and several 10 ml samples were taken throughout the reactions.

Table 3. Experiments 1 and 2: recipes of reactions at 65°C.

	Experiment 1	Experiment 2
Molar comonomers ratio (VBT:VBA)	1:4	1:8
[VBT] \equiv [A] (mol/l)	0.0413	0.0200
[VBA] \equiv [B] (mol/l)	0.1647	0.1649
[Isopropanol] (mol/l)	0.23	0.23
[AIBN] \equiv [I ₂] (mol/l)	0.00307	0.00287

Measurements

All samples were analyzed to determine the comonomers' conversion (x), copolymer molecular weight distribution (MWD), and copolymer average composition.

Conversion was determined by gravimetry. First, an aliquot of each sample was weighted (m_s). Then, the polymer was isolated from isopropanol as follows: (a) 200 ml of acetone containing liquid air were added; (b) the solid precipitate was filtrated and washed with cold acetone; and (c) the polymer was dried under vacuum at room temperature until constant weight (m_p). The comonomers conversion was calculated from:

$$x = \frac{m_p}{m_s(1 - w_{sv}^0)} \quad (2)$$

where w_{sv}^0 is the weight fraction of isopropanol in the recipe (Table 3).

The copolymer MWD and average molecular weights were determined by gel permeation chromatography (GPC). For this purpose, an Agilent 1100 chromatograph was fitted with a set of TSK PW 2500 and 4000 columns and equipped with a differential refractometer. The carrier solvent was a 70/30 buffer mixture of water/methanol containing sodium acetate (0.5 M) and acetic acid (0.5 M) with a flow rate of 1.0 ml/min. The calibration curves were obtained

Table 4. Experiments 1 and 2: copolymer chemical compositions.

Exp. 1			Exp. 2		
x [%]	C/H/N [weight%]	Bounded VBT:VBA (molar)	x [%]	C/H/N [weight%]	Bounded VBT:VBA (molar)
27.4	64.4/9.1/5.9	1:5	29.1	62.0/9.1/5.4	1:8
35.9	62.0/9.0/5.6	1:6	38.9	61.4/9.3/5.2	1:10
47.0	63.1/8.8/5.7	1:5	51.4	62.1/9.3/5.2	1:9
53.0	64.3/9.0/5.9	1:5	63.3	63.5/9.3/5.3	1:10
63.1	65.5/8.8/5.9	1:5	75.2	63.7/9.1/5.4	1:10
67.2	65.2/8.8/5.9	1:5	98.7	63.5/9.1/5.4	1:10
83.0	64.9/8.8/5.9	1:5			
98.4	65.9/8.6/6.0	1:5			

from polyethylene oxide standards dissolved in the same buffer. The data treatment was carried out with Agilent GPC data analysis software.

The average copolymer composition was determined by elemental analysis on an Exeter Analytical 240 analyzer, with the classical modified Pregl/Dumas technique. The measured mass ratios C/N/H were used to calculate the molar ratio VBT/VBA in the copolymer.

Figure 3 presents the measured conversions and average molar masses, and Table 4 presents the average chemical compositions. In Experiment 1, the final conversion of 98% was reached after 20 h. In Experiment 2, the same conversion was reached after 18 h. As expected, the polymerization rate falls at increasing conversions. The average molecular weights fall monotonically along the reaction. The elemental analysis reveals that the ratio of bound VBT:VBA almost coincides with the initial comonomers ratio, indicating near identical reactivities for each of the comonomer radicals.

Conclusions

After some preliminary reactions, two copolymerizations of VBT and VBA were described. Elemental analysis results showed that the copolymer composition remains essentially constant, and that it also corresponds to the initial comonomers ratio. A relatively general mathematical model was developed for simulating a free-radical copolymerization. However, a gross simplification was assumed when adopting common values for all the possible propagations, recombination terminations, and transfer reactions to the comonomers. For this reason, the system reduces to an equivalent homopolymerization. The resulting rate constants of propagation and termination were considerably lower than those of a solution homopolymerization of St. This suggests a

strong effect of the polar and ionic natures of solvent and comonomer pending groups.

In future works, the effect of the solvent, initiator concentration, and temperature on the molecular characteristics of VBT-VBA copolymers will be investigated. Also, the photo-curing process will be considered.

Acknowledgements

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Appendix A: Mathematical model

A.1. Basic module

From the kinetic mechanism of Table 1, the following material balances may be written:

Initiator

$$\frac{d([I_2]V)}{dt} = -k_d[I_2]V \quad (\text{A.1})$$

Comonomers

Assuming the “long chain approximation,” by which monomers are only consumed by propagation reaction, the comonomer molar balances are:

$$\begin{aligned} \frac{d([A]V)}{dt} &= -R_{pA}V \\ &= -\{k_{pAA}[A^\bullet] + k_{pBA}[B^\bullet]\}[A]V \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} \frac{d([B]V)}{dt} &= -R_{pB}V \\ &= -\{k_{pBB}[B^\bullet] + k_{pAB}[A^\bullet]\}[B]V \end{aligned} \quad (\text{A.3})$$

where R_{pA} and R_{pB} are the global rates of comonomers consumption; V is the reaction volume; and $[A^\bullet]$ and $[B^\bullet]$ are the total concentrations of comonomer radicals, with $[A^\bullet] = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} [A_{m,n}^\bullet]$ and $[B^\bullet] = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} [B_{m,n}^\bullet]$.

Radical species

$$\frac{d([R_C^\bullet]V)}{dt} = \{2fk_d[I_2] - k_{iA}[A][R_C^\bullet] - k_{iB}[B][R_C^\bullet]\}V \quad (\text{A.4})$$

where f is the efficiency factor of the chemical initiator.

$$\begin{aligned} \frac{d([A_{1,0}^\bullet]V)}{dt} &= (k_{iA}[R_C^\bullet] + k_{fAA}[A^\bullet] + k_{fBA}[B^\bullet])[A]V \\ &\quad - \{k_{pAA}[A] + k_{pAB}[B] + k_{fAA}[A] \\ &\quad + k_{tAA}[A^\bullet] + k_{tAB}[B^\bullet]\}[A_{1,0}^\bullet]V \end{aligned} \quad (\text{A.5})$$

$$\begin{aligned} \frac{d([A_{m,n}^\bullet]V)}{dt} &= (k_{pAA}[A_{m-1,n}^\bullet] + k_{pBA}[B_{m-1,n}^\bullet])[A]V \\ &\quad - \{k_{pAA}[A] + k_{pAB}[B] + k_{fAA}[A] \\ &\quad + k_{fAB}[B] + k_{tAA}[A^\bullet] + k_{tAB}[B^\bullet]\}[A_{m,n}^\bullet]V \\ &\quad m = 2, 3, \dots, \infty, \quad n = 0, 1, 2, 3, \dots, \infty \end{aligned} \quad (\text{A.6})$$

$$\begin{aligned} \frac{d([B_{0,1}^\bullet]V)}{dt} &= (k_{iB}[R_C^\bullet] + k_{fBB}[B^\bullet] + k_{fAB}[A^\bullet])[B]V \\ &\quad - \{k_{pBB}[B] + k_{pBA}[A] + k_{fBB}[B] + k_{tBB}[B^\bullet] \\ &\quad + k_{tAB}[A^\bullet]\}[B_{0,1}^\bullet]V \end{aligned} \quad (\text{A.7})$$

$$\begin{aligned} \frac{d([B_{m,n}^\bullet]V)}{dt} &= (k_{pBB}[B_{m,n-1}^\bullet] + k_{pAB}[A_{m,n-1}^\bullet])[B]V \\ &\quad - \{k_{pBB}[B] + k_{pBA}[A] + k_{fBB}[B] + k_{fBA}[A] \\ &\quad + k_{tBB}[B^\bullet] + k_{tAB}[A^\bullet]\}[B_{m,n}^\bullet]V \\ &\quad m = 0, 1, 2, 3, \dots, \infty, \quad n = 2, 3, \dots, \infty \end{aligned} \quad (\text{A.8})$$

From Eqs (A.5)–(A.8), the following expressions for the total free macroradicals are obtained:

$$\begin{aligned} \frac{d([A^\bullet]V)}{dt} &= \{k_{iA}[R_C^\bullet] + (k_{pBA} + k_{fBA})[B^\bullet]\}[A]V \\ &\quad - \{(k_{pAB} + k_{fAB})[B] + k_{tAA}[A^\bullet] \\ &\quad + k_{tAB}[B^\bullet]\}[A^\bullet]V \end{aligned} \quad (\text{A.9})$$

$$\begin{aligned} \frac{d([B^\bullet]V)}{dt} &= \{k_{iB}[R_C^\bullet] + (k_{pAB} + k_{fAB})[A^\bullet]\}[B]V \\ &\quad - \{(k_{pBA} + k_{fBA})[A] + k_{tBB}[B^\bullet] \\ &\quad + k_{tAB}[A^\bullet]\}[B^\bullet]V \end{aligned} \quad (\text{A.10})$$

Comonomers conversion

After solving Eqs. (A.1)–(A.4) and (A.9)–(A.10), the conversion is calculated as follows:

$$x = \frac{([A]_0 - [A])M_A + ([B]_0 - [B])M_B}{[A]_0M_A + [B]_0M_B} \quad (\text{A.11})$$

where M_A and M_B are the molar masses of A and B, respectively; and $[A]_0$ and $[B]_0$ are the initial concentrations of A and B, respectively.

A.2. Detailed module

The NCLD of the copolymer is obtained from the kinetic mechanism of Table III as follows:

$$\begin{aligned} \frac{d([C_{m,n}]V)}{dt} = & \{ (k_{fAA}[A_{m,n}^\bullet] + k_{fBA}[B_{m,n}^\bullet])[A] \\ & + (k_{fBB}[B_{m,n}^\bullet] + k_{fAB}[A_{m,n}^\bullet])[B] \\ & + \frac{1}{2} \sum_{r=0}^{m-1} \sum_{q=0}^{n-1} (k_{tAA}[A_{r,q}^\bullet] + k_{tAB}[B_{r,q}^\bullet])[A_{m-r,n-q}^\bullet] \\ & + \frac{1}{2} \sum_{r=0}^{m-1} \sum_{q=0}^{n-1} (k_{tBB}[B_{r,q}^\bullet] + k_{tAB}[A_{r,q}^\bullet]) \\ & \times [B_{m-r,n-q}^\bullet] \} V \\ & m, n = 0, 1, 2, 3 \dots, \infty \quad (\text{A.12}) \end{aligned}$$

Average molecular weights

After solving Eq. (A.12), the average molecular weights of the copolymer are estimated through:

$$\bar{M}_n = \frac{\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} [C_{n,m}](nM_A + mM_B)}{\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} [C_{n,m}]} \quad (\text{A.13})$$

$$\bar{M}_w = \frac{\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} [C_{n,m}](nM_A + mM_B)^2}{\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} [C_{n,m}](nM_A + mM_B)} \quad (\text{A.14})$$