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Linear copolymer chains form in a chain-addition reaction which includes initiation, homopropagation, crosspropagation, and termination by transfer, disproportionation, and combination. Chain growth obeys the Markov property. Multiple types of monomer units are involved; some types have reactive site, others do not. These chains are then crosslinked by a small monomer crosslinker which may be polydispersed. The resulting network consists of soluble, pendant, and elastically effective fractions. Using classical Markov chain analysis techniques, various statistical properties of the polymer chains are computed. The gel point, weight fractions and other network properties can then be computed. The effects of unequal rates of homopropagation and crosspropagation can be observed.

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CALCULATION OF NETWORK PARAMETERS OF CROSSLINKED MARKOVIAN POLYMER CHAINS

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Linear copolymer chains form in a chain-addition reaction which includes initiation, homopropagation, crosspropagation, and termination by transfer, disproportionation, and combination. Chain growth obeys the Markov property. Multiple types of monomer units are involved; some types have reactive sites, others do not. These chains are then crosslinked by a small monomer crosslinker which may be polydispersed. The resulting network consists of soluble, pendant, and elastically effective fractions. Using classical Markov chain analysis techniques, various statistical properties of the polymer chains are computed. The gel point, weight fractions and other network properties can then be computed. The effects of unequal rates of homopropagation and crosspropagation can be observed.

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Introduction

A frequently encountered class of network polymers consists of polymer chains crosslinked via a small monomer crosslinker. It is useful to be able to predict network parameters such as gel point and weight fractions of soluble, pendant and elastically effective material. Probability models can be developed to accomplish this, subject to certain simplifying assumptions.

The purpose of this paper is to extend previous probability models of crosslinking systems to include polymer chains with an arbitrary number of different types of monomer repeat units, some with reactive sites and others without. A Markov model of chain growth is assumed. Certain statistical properties of the polymer chains are needed to compute network parameters of the crosslinked system. These properties are computed using the classical theory of finite-state, transient Markov chains; it is not necessary to resort to Monte Carlo techniques to estimate properties of such general chains.

A network model is based on the three simplifying assumptions of Flory [2] and Stockmayer [8]: (i) functional sites have equal reactivity, (ii) functional sites react independently of one another, and (iii) intramolecular reactions do not occur in the finite species. Using statistical properties of the polymer chains and the crosslinking monomer, the network model computes gel point and network parameters such as weight fractions soluble, pendant, and elastically-effective as a function of conversion. This model shows the effect of unequal rates of homopropagation and crosspropagation in the chain-growth reaction on these network parameters.

A Model of Polymer Chain Growth

Polymer chains are formed from several reactants: initiator, I; transfer agent, TH; monomers, M_k, k=1, 2, . . . m. Chain growth occurs in three stages. During initiation, the initiator I changes into two activated initiators, $I^\bullet$. The activated initiator then reacts with an unreacted monomer, M_k, resulting in a short chain consisting of a reacted initiator, I^r, and an activated monomer, $M_k^\bullet$, k=1, 2, . . . , m. Chain growth consists of the activated chain-ends reacting with unreacted monomers. Chain termination can occur in three ways. Termination by combination occurs when two chains with activated end-monomers combine to form one completed chain. Termination by disproportionation occurs when two chains

with activated end-monomers terminate but do not combine, resulting in two completed chains. Termination by transfer occurs when a live chain-end reacts with a transfer agent, TH; the hydrogen atom completes the chain and the transfer agent is activated, $T^{\bullet}$. The activated transfer agent $T^{\bullet}$ then initiates a new chain by reacting with an unreacted monomer. This chain growth reaction can be represented as

Initiation:	$I \rightarrow 2\, I^{\bullet}$	,	k^{d}
	$I^{\bullet} + M_j \rightarrow I^{r}M_j^{\bullet}$	,	k_j^{ii}
	$T^{\bullet} + M_j \rightarrow T^{r}M_j^{\bullet}$	,	k_j^{ti}
Growth:	$\sim M_i^{\bullet} + M_j \rightarrow \sim M_i^{r}M_j^{\bullet}$	,	k_{ij}^{gr}
Termination:	$\sim M_i^{\bullet} + \cdot \rightarrow \sim M_i^{r}M_j^{r}\sim$	,	k_{ij}^{tc}
	$\sim M_i^{\bullet} + \sim M_j^{\bullet} \rightarrow \sim M_i^{r} + \sim M_j^{r}$,		k_{ij}^{td}
	$\sim M_i^{\bullet} + TH \rightarrow \sim M_i^{r}H + T^{\bullet}$,		k_i^{tr}

for i, j = 1, 2. . . . , m, where the k's represent kinetic rates. This, and similar, chain growth reactions are described by Williams [9], Odian [7], Galbraith, et al. [3], and others. A system of kinetic equations based on the above scheme with second order kinetics can be defined and solved (by numerical integration). This yields concentrations (or numbers) of I, I^{r} , $T^{\bullet}$, T^{r}, H, M_k, $M_k^{\bullet}$, M_k^{r}, k=1, 2, . . . , m, as a function of time. This system consists of 3m + 7 differential equations.

It is assumed that the above system is stiff: the rate at which activated initiator is introduced into the system is much less than the rates of chain growth and termination. This means that the chains initiated during a short time interval (of length Δt) will see a constant environment while growing; the salient aspects of this environment are the concentrations of TH, M_k and $M_k^{\bullet}$, k=1, 2, . . . , m. This constant environment and the kinetic growth which depends on just the last unit of a live chain lead to a Markov model of chain composition for the chains initiated

during the interval. Chains from other intervals will also have Markov models, but with different parameters. The totality of chains produced will correspond to a mixture of Markov models. Mixing destroys the Markov property; thus, the solution approach consists of computing the statistical chain parameters needed for network analysis for a succession of short time intervals using the Markov model and parameters for that interval, and then taking the mixture of the chains and parameters. The number of chains initiated by $I^\bullet$ and $T^\bullet$ during a short interval of length Δt can be represented by ΔI^r and ΔT^r, respectively. These values and the current values of TH, M_k, and $M_k^\bullet$ uniquely determine the polymer chains initiated during the time interval.

Instantaneous Markov Model of Chain Composition

Consider the polymer chains initiated in a short time interval, focusing on the portion between initiation and termination. Each position can be filled by different elements. The initiating elements may be I or T. Interior elements may be M_k, $k=1, 2, \ldots, m$. The terminating element may be H, or phantom elements D, or C_k, $k=1, 2, \ldots, m$, where D represents termination by disproportionation and C_k represents termination by combination with $M_k^\bullet$, $k=1, 2, \ldots, m$. Let $\underset{\sim}{X} = (X_0, X_1, X_2, \ldots, X_T)$ represent the polymer chain; $\underset{\sim}{X}$ is a transient Markov chain with initial distribution $\underset{\sim}{\pi}_0$ and transition probability matrix $P_r(\cdot, \cdot)$, where the subscript "r" represents "right", i.e., the chain is envisioned growing to the right. The initial distribution is

$$\pi_0(I) = P(X_0 = I) = \Delta I^r/(\Delta I^r + \Delta T^r)$$

$$\pi_0(T) = P(X_0 = T) = \Delta T^r/(\Delta I^r + \Delta T^r).$$

The transition probabilities $P_r(u, v) = P(X_{i+1} = v | X_i = u)$ are defined for $u \in \{M_1, \ldots, M_m, I, T\}$ and $v \in \{M_1, \ldots, M_m, H, D, C_1, \ldots, C_m\}$. They are computed from kinetic rates and the instantaneous concentrations of TH, M_k, and $M_k^\bullet$, $k=1, 2, \ldots, m$. For example,

$$P_r(I, M_j) = k_j^{ii}[M_j]_t / \sum_{j=1}^{m} k_j^{ii}[M_j]_t.$$

This model describes polymer chain structure between initiation and termination.

Now consider the chains which terminate by combination. A chain ending in a phantom state C_k is actually combined with a chain component ending with M_k. This component is viewed in the "left" direction, i.e., the structure is seen looking toward the initiator, rather than away from it. The Markov property still holds but the index set for the chain is reversed. Let $P_\ell(\cdot\ ,\ \cdot)$ be the transition matrix of the reversed chain, the subscript "ℓ" denoting the direction "left," toward the initiating units. The reversed transition probabilities $P_\ell(u, v)$ are defined for $u \in (M_1, \ldots, M_m, H)$ and $v \in (M_1, \ldots, M_m, I, T)$. P_ℓ can be computed from $\underset{\sim}{\pi}_0$ and P_r. Feller [1] and Kemeny and Snell [4] are recommended references for the necessary background on Markov chains.

The initial distribution $\underset{\sim}{\pi}_0$ and the transition matrices P_r and P_ℓ could be used for Monte Carlo generation of a statistical sample of chains formed during the current short time interval. Note, however, that chains terminating by combination have two initiators and in effect will be counted twice; so the statistical sample must be adjusted accordingly.

The Network Model

The chains produced in the above reaction are crosslinked by reacting them with a small monomer crosslinker, B_g. It is assumed that chain monomer-units M_k, $k=1, 2, \ldots, nf$, each have a reactive site, denoted as an A-site. None of the other chain units have reactive sites.

Miller and Macosko [5] present a network model for crosslinking polydispersed chains. Their equation (107) for the gel point is valid for the current system:

$$\alpha_c = [r(E_sF_A-1)\ (E_sF_B-1)]^{-1/2},$$

where r is the stoichiometric imbalance and E_sF_A equals the expected functionality of a chain chosen randomly by picking a reactive site. Their analyses is based on the quantities $P(F_A^{out})$ and $P(F_B^{out})$ which are solutions of the equations:

$$P(F_A^{out}) = 1 - \alpha + \alpha \sum_{f=0}^{\infty} (P(F_B^{out}))^f\ P_s(F_A - 1 = f)$$

$$P(F_B^{out}) = 1 - r\alpha + r\alpha \sum_{g=0}^{\infty} (P(F_A^{out}))^g\ P_s(F_B - 1 = g).$$

These equations are also valid for the current system.

For general chains, additional modelling is required for computation of weight fraction soluble, pendant and elastically-effective. From any repeat unit on a chain, it is important to know the network structure looking "left" and "right" along the chain. Let D_ℓ represent the event of pendant (dangling) material to the left, D_r pendant to the right, and $D_b = D_\ell \cap D_r$ pendant in both directions. For a particular repeat unit M_i, the probabilities of these events are

$$P(D_d|M_i) = \sum_{f=0}^{\infty} (P(F_A^{out}))^f \, P(F_x = f|M_i)$$

for $d = r, \ell, b$; where F_r, F_ℓ, F_b are random variables representing the number of functional sites seen when looking "right," "left," and in "both" directions from a repeat unit M_i, $i=1, 2, \ldots, m$; and from I, T, and H. For $i=1, 2, \ldots, nf$, the monomer units have A-sites; thus

$$P(M_i \text{ soluble}) = P(F_A^{out}) \, P(D_b|M_i)$$

$$P(M_i \text{ pendant}) = (1 - P(F_A^{out})) \, P(D_b|M_i) + P(F_A^{out})(P(D_r|M_i) + P(D_\ell|M_i) - 2P(D_b|M_i))$$

$$P(M_i \text{ effective}) = 1 - P(M_i \text{ soluble}) - P(M_i \text{ pendant}).$$

For $i = nf+1, \ldots, m$, the monomer units have no sites; thus

$$P(M_i \text{ soluble}) = P(D_b|M_i)$$

$$P(M_i \text{ pendant}) = P(D_r|M_i) + P(D_\ell|M_i) - 2P(D_b|M_i)$$

$$P(M_i \text{ effective}) = 1 - P(M_i \text{ soluble}) - P(M_i \text{ pendant}).$$

Similar equations hold for I, T, and H. The above equations can be combined to compute overall weight fraction of soluble, pendant, and elastically-effective chain material. Using the above equations and the appropriate theory from [5], network

weight fractions and gel point can be computed, provided the distributions of functionality to the right, left, and both directions from each unit are available.

Functionality to the Right and Left

Let F_ℓ equal the functionality to the left of a chain unit, M_i, say. Consider the Markov chain looking left which ignores M_k without sites ($k = nf+1, \ldots, m$). Denote the chain by $\underset{\sim}{Y} = (Y_0, Y_1, \ldots, Y_T)$; where Y_0 equals M_i, the starting point, and Y_T equals I or T, the terminations looking left. The transition matrix $P^f_\ell(u, v)$ is defined for $u \in \{M_1, \ldots, M_m, H\}$ and $v \in \{M_1, \ldots, M_{nf}, I, T\}$, and can be computed from P_ℓ using the concept of absorption probabilities for Markov chains. The distribution of F_ℓ is related to $\underset{\sim}{Y}$:

$$P(F_\ell = f|M_i) = P(Y_{f+1} = I \text{ or } T|Y_0 = M_i),$$

which can be computed from P^f_ℓ. Denote this conditional distribution as $\mathcal{L}(F_\ell|M_i)$, for $i = 1, \ldots, m$; and also for H.

Now consider functionality to the right, F_r. This is more complicated because of the possibility of termination by combination. Let F^o_r equal the functionality on the original chain, and let F^c_r equal the functionality on the continuation added by termination by combination. Consider the Markov chain $\underset{\sim}{Z} = (Z_0, Z_1, \ldots, Z_T)$ of monomer units with functional sites to the right until termination; the termination state Z_T may be H, D, or C_k, $k = 1, 2, \ldots, m$. The transition matrix $P^f_r(u, v)$ is defined for $u \in \{M_1, \ldots, M_m, I, T\}$ and $v \in \{M_1, \ldots, M_{nf}, H, D, C_1, \ldots, C_m\}$ and can be computed from P_r. The conditional distribution of F^o_r given the termination state is related to $\underset{\sim}{Z}$:

$$P(F^o_r = f|M_i, C_k) = P(Z_{f+1} = C_k|Z_0 = M_i)/P(C_k|M_i)$$

where

$$P(C_k|M_i) = \sum_{f=0}^{\infty} P(Z_{f+1} = C_k|Z_0 = M_i),$$

which can be computed from P^f_r. Denote this conditional distribution as $\mathcal{L}(F^o_r|M_i, C_k)$ for $i, k = 1, 2, \ldots, m$; and similarly for I and T, initial states.

Suppose the additional functionality to the right results through termination with phantom state C_k; this is equivalent to looking left from M_k, which may or may not contain a functional site itself. So

$$\mathcal{L}(F_r^c|M_i, C_k) = \mathcal{L}(F_r^c|C_k) = \begin{cases} \mathcal{L}(1+F_\ell|M_k) & k=1, \ldots, nf \\ \mathcal{L}(F_\ell|M_k) & k=nf+1, \ldots, m \end{cases}.$$

Combining the functionality of the two parts of the chain to the right gives

$$\mathcal{L}(F_r|M_i) = \sum_{k=1}^{m} \mathcal{L}(F_r^o|M_i, C_k) * \mathcal{L}(F_r^c|C_k)\, P(C_k|M_i)$$

$$+ \mathcal{L}(F_r^o|M_i, H)\, P(H|M_i) + \mathcal{L}(F_r^o|M_i, D)\, P(D|M_i)$$

where "*" represents the convolution of probability distributions.

For chains produced in a short time interval, F_r and F_ℓ are conditionally independent given the starting segment. Thus the sum in both directions is obtained by convolution:

$$\mathcal{L}(F_b|M_i) = \mathcal{L}(F_\ell|M_i) * \mathcal{L}(F_r|M_i),$$

$i=1, 2, \ldots, m$.

Mixtures of Polymer Chains

The above probability laws for functionalities to the right, to the left and in both directions from chain repeat units are for the chains produced in a short interval of time: $(t, t+dt)$. The probability law for the totality of chains is the mixture of the laws for the short intervals. Suppose $\mathcal{L}_t(F_x|M_i)$ is the law for chains produced in $(t, t+dt)$ and $dM_i(t)$ equals the number of M_i monomers reacted in $(t, t+dt)$. Then, if the reaction runs over $(0, S)$, the probability laws for functionality are given by

$$\overline{\mathcal{L}}(F_d|M_i) = \int_0^S \mathcal{L}_t(F_d|M_i)dM_i(t) \Big/ \int_0^S dM_i(t)$$

for d=r, ℓ, b, and i=1, 2, . . . , m. Similar equations hold for I, H, T. These are the distributions needed for computation of weight fractions soluble, pendant, and effective. The distribution of $F_A - 1$ needed for the gel point is obtained by mixing $\overline{\ell}(F_b|M_i)$, i=1, . . . , nf.

A Computational Example

The following system is a variation of one in [5]. Polymer chains have two types of repeat units: the first has a reactive site, the second does not. Elements have the following masses: $M_1 = 146$; $M_2 = 142$; I = 50; T = 75; H = 1. The kinetic rates: $k^d = .01$; $k_1^u = k_2^u = 2.0$; $k_1^{ti} = k_2^{ti} = 4.0$; $k_1^{tr} = k_2^{tr} = 8.0$; $k_{11}^{tc} = k_{12}^{tc} = k_{21}^{tc} = k_{22}^{tc} = 6.0$; $k_{11}^{td} = k_{12}^{td} = k_{21}^{td} = k_{22}^{td} = 4.0$; $k_{11}^{gr} = k_{12}^{gr} = k_{21}^{gr} = k_{22}^{gr} = 1.0$. (This system has equal rates of homopropagation and crosspropagation.) Moles of initial reactants: I = 1.0; TH = 2.0; $M_1 = 50.0$; $M_2 = 50.0$. The reaction went for a time duration of 1.50 time units. The solution of the kinetic equations was done in three time intervals, using a simple-minded difference equation approximation with a step size of 0.001 time units. The resulting chains had a number-average number of 7.43 monomer units and a number-average functionality of 3.72.

These polymer chains were then reacted with a small B_g crosslinker. This monomer was polydispersed, consisting of B_2, B_3, and B_4 units which had weights 168, 478, and 788, respectively, and mole fractions 0.3, 0.4 and 0.3, respectively. The mass of the reactants: mass of A-chains = 1000.00, mass of B-monomers = 600.00. There was a stoichiometric imbalance: r = .862. The site-average functionalities are $E_S(F_A) = 7.43$ and $E_S(F_B) = 3.20$, which gives a gel point: $\alpha_c = 0.286$. The weight fractions of soluble, pendant, and elastically effective material are shown in Figure 1 by the solid lines and referred to as System I.

In order to investigate the effect of unequal rates of homopropagation and crosspropagation, two additional chains systems were computed. Both systems are identical to the above system except for chain-growth rates. System II has faster homopropagation: $k_{11}^{gr} = k_{22}^{gr} = 1.9$, $k_{12}^{gr} = k_{21}^{gr} = 0.1$. System III has faster crosspropagation: $k_{11}^{gr} = k_{22}^{gr} = 0.1$, $k_{12}^{gr} = k_{21}^{gr} = 1.9$. Both of these systems yielded chains with identical number average length (7.43) and functionality (3.72) as before. In System II (homopropagation ≫ crosspropagation) $E_S(F_A) = 10.95$

and $\alpha_c = 0.230$, a significant change from before. In System III (homopropagation $\ll$ crosspropagation) $E_s(F_A) = 7.00$ and $\alpha_c = 0.296$, not much change. The weight fractions for System II are shown in Figure 1. The weight fractions for System III do not differ much from System I (homopropagation = crosspropagation).

Conclusions

A model based on Markovian chain growth has been developed which shows that Monte Carlo methods are not required for analyzing crosslinked systems of such chains. The model has been programmed in WATFIV and runs quite fast (the examples of the previous section each required 17 seconds to compile and run on an IBM 4381). Preliminary investigations show that unequal rates of homopropagation and crosspropagation can significantly affect network parameters. A detailed description of an extended version of this model and analysis is in preparation [6]. It will include pre-gel molecular parameters, multiple types of unequally reactive sites on chains, additional chain-forming mechanisms, and other topics.

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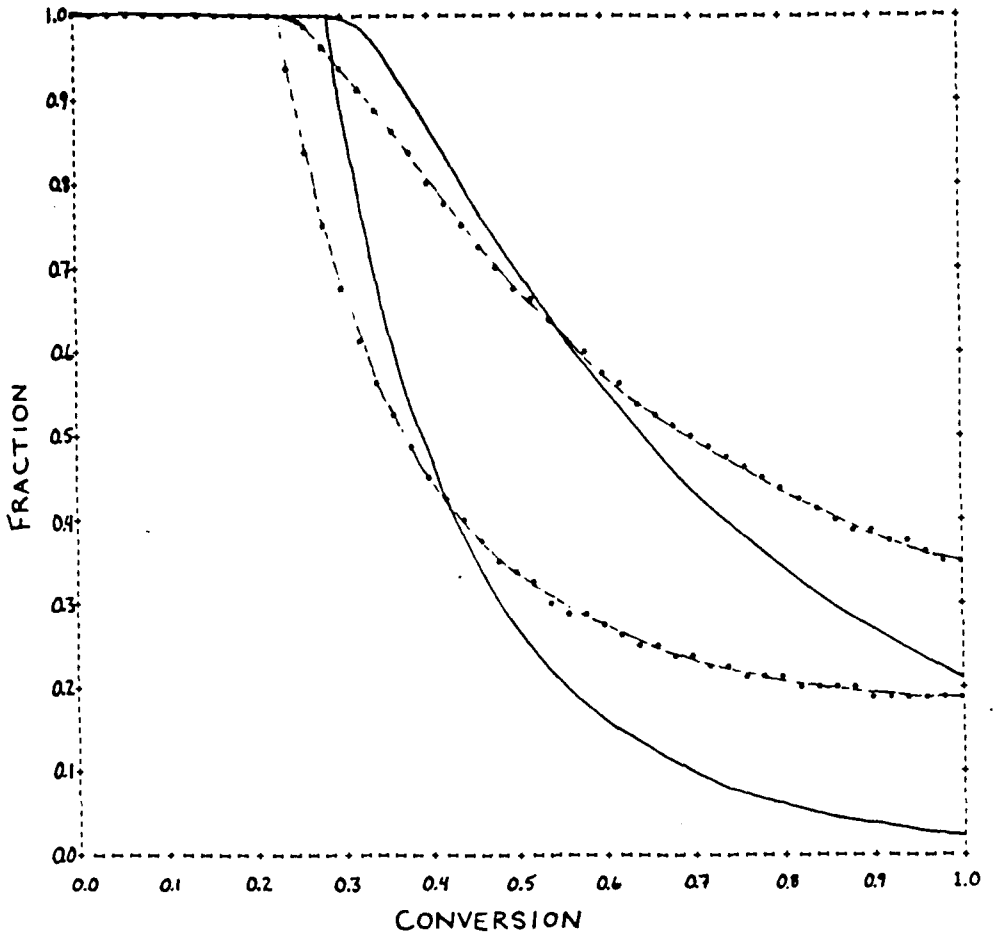

Figure 1. Weight fractions of soluble, pendant, and effective material for two different crosslinking systems as a function of conversion. The solid lines represent System I, an ideal system (equal rates of chain homopropagation and crosspropagation). The dotted lines represent System II, a system with much greater homopropagation rate than crosspropagation rate. The lower curves represent weight fraction soluble. The differences between the two curves represent weight fraction pendant. The differences between the upper axis and the upper curves represent weight fraction of elastically effective material.