An exactly solvable model of polymerization

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ABSTRACT

This paper considers the evolution of a polydisperse polymerizing system comprising $g_1, g_2 \ldots$ – mers carrying $\phi_1, \phi_2 \ldots$ functional groups reacting with one another and binding the g-mers. In addition, the g-mers are assumed to be added at random by one at a time with a known rate depending on their mass g and functionality ϕ. Assuming that the rate of binding of two g-mers is proportional to the product of the numbers of nonreacted functional groups the kinetic equation for the distribution of clusters (g-mers) over their mass and functionalities is formulated and then solved by applying the generating function method. In contrast to existing approaches this kinetic equation operates with the efficiencies proportional to the product of the numbers of active functional groups in the clusters rather than to the product of their masses. The evolution process is shown to reveal a phase transition: the emergence of a giant linked cluster (the gel) whose mass is comparable to the total mass of the whole polymerizing system. The time dependence of the moments of the distribution of linked components over their masses and functionalities is investigated. The polymerization process terminates by forming a residual spectrum of sol particles in addition to the gel.

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1. Introduction

The coalescence processes play the central role in many physical and physicochemical processes. A hundred years ago Smoluchowski [1] formulated his salient equation that describes the coagulation process in aerosols. Since then the Smoluchowski approach found wide applications in numerous areas of physics, chemistry, economy, epidemiology, and many other branches of science [2–11]. Among them is the physics of polymers where the coalescence processes are almost entirely responsible for the dynamics of polymerization [12–15].

The most widespread model of polymerization (the Flory model [4]) considers monomeric units carrying f functional centers that can react with each other losing their activity after a coalescence act. It is clear that if $f \geq 3$ the coalescing monomers form ramified structures. The dynamics of this process is commonly accepted to be described in terms of particle mass spectrum $c(g,t)$ (the number concentrations of g-mers in the coagulating system) [7–10]. The spectrum obeys the Smoluchowski equation,

$$\frac{dc(g,t)}{dt} = I(g,t) + \frac{1}{2}\sum_{l=1}^{g-1} K(g-l,l)c(g-l,t)c(l,t)$$

$$-c(g,t)\sum_{l=1}^{\infty} K(g,l)c(l,t). \tag{1}$$

Here g and l are the particle masses in units of a monomeric mass. This equation is a consequence of a simple balance principle: the increase in g-particle concentration $c_g(t)$ comes from the coalescence of $g - l$ and l-particles (the first term on the right-hand side (RHS) of this equation). The second term describes the consumption of g-particle by all other participants of the coagulation process and thus enters with the negative sign. The coagulation kernel $K(g,l)$ is the rate of coalescence of the particles containing g and l monomers. The first term $I(g,t)$ on the right-hand side (RHS) of this equation is the source of g-mers (the volume rate of g-mers production).

In Ref. [9] the authors applied Eq. (1) for describing the kinetics of free (no source, $I(g,t)=0$) polymerization of tree–like structures. In this model the functionality of a tree–like cluster is connected with the functionality f of each graph vertex: $\phi = g(f-2)+2$ and the coagulation kernel is proportional to the product of the colliding clusters functionality (see, e.g., [9]),

$$K(g_1,g_2) \propto [g_1(f-2)+2][g_2(f-2)+2] \tag{2}$$

In this paper we consider the evolution of a polydisperse system of clusters comprising g-mers each of which carries ϕ functional groups. Each cluster is now characterized by two *independent* integers: its mass g in units of a monomer mass and functionality ϕ.

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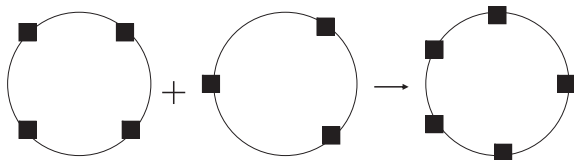
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Fig. 1. Two particles of masses g_1 and g_2 and functionalities ϕ_1 and ϕ_2 coalesce owing to their active centers (black squares) annihilate. Each coalescence act conserves the total mass of the particles $(g = g_1 + g_2)$ and diminishes its total functionality by two: $(\phi = \phi_1 + \phi_2 - 2)$

The clusters move, collide and coalesce producing a daughter cluster. Only binary collisions are taken into account, It is assumed that the coalescence results from the interaction of two functional centers located at different clusters. The centers die out on reacting. The polymerization process thus develops along the scheme shown in Fig. 1,
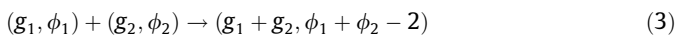
$$(g_1, \phi_1) + (g_2, \phi_2) \rightarrow (g_1 + g_2, \phi_1 + \phi_2 - 2) \tag{3}$$

In addition, the g-mers are assumed to be added at random by one at a time with a known rate depending on their mass g and functionality ϕ. Assuming that the rate of binding of two g-mers is proportional to the product of the numbers of nonreacted functional groups

$$K(g_1, \phi_1 | g_2, \phi_2) \propto \phi_1, \phi_2 \tag{4}$$

the kinetic equation for the distribution of clusters (g-mers) over their mass and functionalities is formulated and then solved by applying the generating function method. In contrast to existing approaches this kinetic equation operates with the efficiencies proportional to the product of the numbers of active functional groups in the clusters rather than to the product of their masses. The evolution process is shown to reveal a phase transition: the emergence of a giant linked cluster (the gel) whose mass is comparable to the total mass of the whole polymerizing system. The time dependence of the moments of the distribution of linked components over their masses and functionalities is investigated. The polymerization process terminates by forming a residual spectrum of sol particles in addition to the gel.

This approach has been applied in Refs [16–18] for considering the kinetics of coalescence of random graphs.

The paper is organized as follows. In the next Section the basic equation and the initial conditions are formulated. In contrast to the Smoluchowski equation the dynamics of polymerization is now governed by the product of the functionalities of two reacting clusters rather than their masses. Although the cluster masses may limit the ranges of changes to the cluster functionality, a unique mass – functionality correlation is not assumed. In Section III this kinetic equation is reformulated in terms of the bivariate generating function. This equation is then solved exactly for zero initial conditions. The precritical and postcritical time behavior of the moments of mass–functionality distribution is investigated in Sect. IV, where the critical time for the sol–gel transition is found and expressed via the moments of the initial mass – functionality distribution and the source function. The critical behavior of the mass–functionality spectrum is investigated in Sect. V. The exact expression for the bivariate generating function of the residual $(t \rightarrow \infty)$ mass – functionality distribution is derived in Sect. VI. In Sections VII and VIII the results are summarized and discussed.

2. Basic equations

Let us imagine a collection of particles of masses $g_1, g_2 \ldots$ carrying $\phi_1, \phi_2 \ldots$ functional centers (g, ϕ are nonnegative integers) that are able to bind two units in one. The functional centers die in this process and their number diminishes by two. A new daughter particle carrying $\phi_1 + \phi_2 - 2$ functional centers results from this coalescence process (see Fig. 1). After a time the next particle joins to this cluster. The process proceeds in this way, and the collection of particles converts to a collection of clusters each of which is characterized by its total mass g (the number of monomers in it) and total functionality ϕ. The clusters move chaotically. collide, and grow as time goes ahead.

The polymerization can be considered as a chain of coalescences of the couples of smaller clusters. In contrast to commonly known coagulation process, each elementary polymerization act diminishes the functionality of the cluster by two. The rate of coalescence is assumed to be independent of the masses of colliding clusters. This process is represented by the scheme Eq. (3), In parallel to coalescence, another process (the source) adds clusters by one with the rate $I(g, \phi)$.

The probability of coalescence is considered to be proportional to the product of total functionalities of two coalescing clusters. In the process of coalescence the functionality of each linked cluster changes. The kinetic equation that governs the dynamics of polymerization looks as follows:

$$\frac{dc(g, \phi; t)}{dt} = I(g, \phi) + \frac{\varkappa}{2} \sum_{l, \eta} (\phi - \eta + 1)(\eta + 1)c(g - l, \phi - \eta + 1; t)$$
$$\times c(l, \eta + 1; t) - \varkappa \phi c(g, \phi; t) \sum_{l, \eta} \eta c(l, \eta; t). \tag{5}$$

Here $\varkappa$ is the coagulation rate constant, $I(g, \phi)$ is the productivity of g-mers with functionality ϕ, $c(g, \phi; t)$ is the concentrations of coalescing clusters. The summations on the RHS of this equation over go over all positive integers g, ϕ.

In what follows we will measure the concentration in units $\sqrt{I_{0,0}/\varkappa}$, time in units $1/\sqrt{\varkappa I_{0,0}}$, and I in units $I_{0,0} = \sum_{g,\phi} I(g, \phi)$. This choice of units makes all variables and unknown function dimensionless and allows us to put $\kappa = 1$ in Eq. (5).

Eq. (5) should be supplemented with the initial conditions,

$$c(g, \phi; t = 0) = c_0(g, \phi). \tag{6}$$

wherever possible, we consider arbitrary initial conditions, $c(g, \phi; 0) = c_0(g, \phi)$ and arbitrary source function $I(g, \phi)$. Some results are found for zero initial conditions and a separable source function $I(g, \phi) = A(g)B(\phi)$.

3. Generating function

We introduce bivariate generating functions for $c(g, \phi; t)$ and for $I(g, \phi)$,

$$\mathcal{F}(z, \xi; t) = \sum_{g, \phi} c(g, \phi; t) z^g \xi^\phi \tag{7}$$

$$\mathcal{I}(z, \xi) = \sum_{g, \phi} I(g, \phi) z^g \xi^\phi. \tag{8}$$

The moments of the distributions $c(g, \phi; t)$ and $I(g, \phi)$ are defined as follows:

$$M_{m,n}(t) = \sum_{g, \phi} g^m \phi^n c(g, \phi; t), \quad I_{m,n} = \sum_{g, \phi} g^m \phi^n I(g, \phi). \tag{9}$$

On multiplying both sides of Eq. (5) by $z^g \xi^\phi$ and summing over all g and ϕ give the equation for $\mathcal{F}$,

$$\dot{\mathcal{F}} = \mathcal{I} + \frac{1}{2} (\mathcal{F}_\xi)^2 - \xi \Phi(t) \mathcal{F}_\xi. \tag{10}$$

Here and everywhere below subscripts ξ, z stand for the derivatives over these arguments, and overdot denotes the derivative over time. Next,