Monte Carlo Studies of Polymer-Chain Dimensions in the Melt in Two Dimensions

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ABSTRACT: When pseudokinetic bond-breaking rearrangements are used, a polymer melt is simulated on a three-way quadratic lattice at a volume fraction of unity. The scaling laws for the root mean square (rms) end-to-end distance, $\langle r^2\rangle^{1/2}$, and the rms gyration radius, $\langle s^2\rangle^{1/2}$, are calculated as a function of chain length, N: $\langle r^2\rangle^{1/2} = (N-1)^{\nu}$, $\langle s^2\rangle^{1/2} = (N-1)^{\nu}$. For a melt with an average chain length of 400, an exponent of 0.54–0.55 is found, which seems to decrease further with increasing average chain length. Different kinetic schemes and different constraints on chain lengths and their influence on chain dimensions are discussed. Melts on a lattice with a thickness of two segments in the z direction have also been studied, and the results are found to be qualitatively similar to those obtained for the two-dimensional monolayer.

Introduction

Flory has postulated that polymer chains in the melt scale like a pseudoideal Θ chain.[1-3] In three dimensions, this Flory theorem has qualitatively been confirmed by experimental studies.[4,5] Kremer[6] with Monte Carlo investigations on a diamond lattice confirmed the Flory theorem for chain lengths, N, up to 200. He also found that at a volume fraction of 0.344 the root mean square (rms) end-to-end distance scales already ideally: $\langle r^2\rangle^{1/2} = (N-1)^{\nu}$, $\nu = 0.50 \pm 0.01$. With pseudokinetic bond-breaking rearrangements,[7-9] which allow Monte Carlo simulations at a volume fraction of unity, Olaj and Lantschbauer[8] and Mansfield[9] investigated melts on a cubic lattice and found for chain lengths up to 512 a slightly larger exponent for the scaling relation of the rms end-to-end distance than the ideal value of $\nu = {}^1/_2$: $\nu = 0.51$–0.52. The bond-breaking rearrangements a priori do not permit the simulation of monodisperse molecular weight distributions, but since Olaj and Lantschbauer[8] found that the exponent does not change with narrowing of the distribution, this slight deviation from ideality is probably not due to the polydispersity of the sample. With the collective motion algorithm, which permits Monte Carlo studies of monodisperse samples at a volume fraction of unity, Pakula and Geyler[10] found also an exponent slightly larger than ${}^1/_2$; i.e., $\nu = 0.5075$. It is not clear as yet whether this small discrepancy is due to the finite chain lengths used in the simulations.

In two dimensions even for the Θ state quite conflicting results have been obtained by experiments, Monte Carlo simulations, and theoretical treatments, and estimated exponents range from $\nu_\Theta = 0.505$ to $\nu_\Theta = 0.57$; see, for instance, Vilanove et al.,[11] Bishop,[12] and Douglas et al.[13] and references therein. These authors point out that the two-dimensional case is more complicated than the three-dimensional one. de Gennes[3] has predicted that chains in a two-dimensional melt are not expected to behave ideally and that they should be more segregated than in three dimensions. Baumgärtner[14] with Monte Carlo studies showed for chain lengths up to 59 and a volume fraction of ${}^5/_6$ that chain dimensions scale with an exponent of about ${}^1/_2$ but that the chains are more swollen than expected from the simple random flight model. He also confirmed that the chains are segregated. A scaling exponent of about ${}^1/_2$ has also been found by Carmesin and Kremer[15] with the bond fluctuation method[16] at volume fractions of 0.4–0.8. Using the magnet polymer analogy, Petschek and Pfeuty[17] calculated that two-dimensional melt chains, which can cross, scale with an exponent ${}^1/_2$ and a preexponential logarithmic correction factor while Saleur[18] found an exponent of ${}^1/_2$ for noncrossing chains.

In this work we want to study the scaling relations of the rms end-to-end distance and the rms gyration radius of an athermal melt on a quadratic lattice at a volume fraction of unity using the pseudokinetic bond-breaking rearrangements.

Monte Carlo Simulation

The pseudokinetic bond-breaking rearrangements we use are those introduced by Olaj et al.[7,8] and by Mansfield.[9] For intermolecular rearrangements we use dimerization and cleavage, substitution reactions, and the metathesis reaction,[8] and for intramolecular rearrangements we use the backbite reaction[9] and cyclization and cleavage.[19] The coding is similar to that described by Madden.[19] We use a quadratic lattice (xl, yl) with periodic boundary conditions. In some runs we use a two-dimensional layer with the dimensions (xl, yl, $zl = 2$) with periodic boundary conditions in the x and y directions and hard walls at the z boundaries. The lattice is stored as a linear array. For each lattice position the chain and segment number of the occupying chain segment and the addresses of the two covalently bound segments are stored. If the lattice position is occupied by an end segment, one of these addresses is zero. The neighbor addresses of each lattice position are stored in a separate array. For each chain the end positions and its length are stored. Every lattice position is occupied by a segment.

An end segment and one of its neighboring lattice positions other than that occupied by the segment covalently bound to the end segment are chosen randomly. If a rearrangement is possible with the chosen pair, it is performed, otherwise the old configuration is retained. This kinetic scheme is used in most calculations, and we call it the natural kinetic scheme. In some runs a different strategy is used. An end segment and a neighbor are again chosen at random, but if the pair permits an intramolecular rearrangement, it is performed and then another random neighbor for one of the end segments of the same chain is chosen until a pair suitable for an intermolecular rearrangement is found or until the procedure is repeated a prespecified number of times. Since with this method chain ends have a more equal probability to participate in an intermolecular rearrangement independent of the conformation, we call it EP for equal probability. For the metathesis a neighboring pair of segments is chosen randomly, and if a metathesis reaction is possible, it is done. The ratio of selected end segments to total number of selected segments is chosen such that metathesis reactions occur about as often as intermolecular rearrangements involving end segments. Intermolecular rearrangements may change the length of the reacting chains, and in

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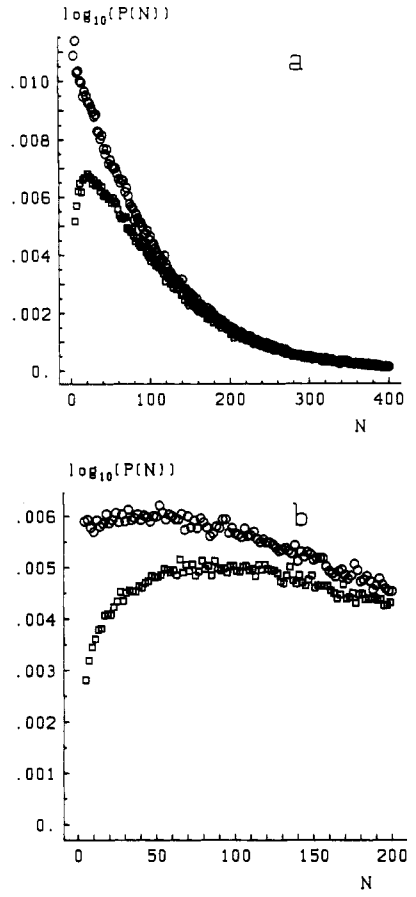

Figure 1. Distributions for $\langle N \rangle = 100$; see also Tables I and II. Chains were forced to be larger than 4 (a) or to fall into the interval $4 \leq N \leq 200$ (b). In both cases only chains from the interval $4 \leq N \leq 200$ are shown. At smaller chain lengths, chains with an even number of segments (○) are more frequent than chains with an odd number of segments (□).

principle any distribution of chain lengths can be selected at this point. Either we use almost no constraint on the chain length distribution, or we force the chains to fall in a symmetric interval about $\langle N \rangle$ as proposed by Madden[19] or to be narrowly distributed around $\langle N \rangle$ as proposed by Olaj and Lantschbauer,[8] where $\langle N \rangle$ is the number-average chain length. In contrast to three dimensions, we find that in two dimensions the results are quite sensitive to the constraint on chain length, see below.

A total of 400 intermolecular rearrangements per segment are enough to equilibrate the melt, and in some cases we have used over 1000. Chain properties were measured every 0.02–0.2 intermolecular rearrangements per segment. Since we do not know the autocorrelation times for the simulation we do not give error bounds, but from independent runs it is seen that the relative random error of the exponents in Table I is less than 0.5%.

Results and Discussion

We did calculations for four different number averages ranging from 25 to 400, and for the number average of 100 we used various constraints for the chain lengths and two kinetic schemes. The results are displayed in Tables I and II. We first discuss the kinetic schemes and the influence of different constraints on the chain lengths.

In Figure 1 we show the distributions obtained for a number-average chain length of 100, either where almost no constraint was used, Figure 1a, or where the chains were forced to fall in the interval $4 \leq N \leq 200$, Figure 1b. The distribution in Figure 1a is qualitatively similar to the most probable distribution, while in the distribution in Figure 1b chains larger than 100 are more frequent than in Figure 1a because of the barrier at $N = 200$. The weight-average to number-average ratio for the distribution in Figure 1a is 1.8, Table I, which is still smaller than the ratio of 2.0 expected for a most probable distribution, and it is only 1.33 for the distribution in Figure 1b. There is a pronounced oscillation in frequency: chains with an even number of segments, or an odd number of bonds, are more frequent than chains with an odd number of segments.

Table I
Scaling Relations $A^*(N-1)^\nu$

	$\langle r^2 \rangle^{1/2}$			$\langle s^2 \rangle^{1/2}$		
$\langle N \rangle$	A	ν		A	ν	$\langle N^2 \rangle / \langle N \rangle$
100[a]	1.034	0.565		0.468	0.554	1.31
100[a,e]	1.175	0.539		0.486	0.545	1.33
100[b]	0.959	0.581		0.450	0.562	1.08
100[c]	0.959	0.581		0.452	0.561	1.04
100[d,i]	0.942	0.585		0.446	0.564	1.01
100[a,b]		0.569			0.557	1.32
100[b,h]		0.571			0.564	1.08
100[c,h]		0.570			0.564	1.04
25	1.039	0.586		0.461	0.571	1.72
100	1.035	0.564		0.466	0.554	1.80
$\langle r_x^2 \rangle^{1/2}$	0.732	0.564	$\langle s_x^2 \rangle^{1/2}$	0.330	0.554	
$\langle r_y^2 \rangle^{1/2}$	0.731	0.563	$\langle s_y^2 \rangle^{1/2}$	0.329	0.555	
200[f]	1.028	0.557		0.471	0.547	1.80
400[g]	1.029	0.549		0.479	0.538	1.76

[a,b] Lattice size is $(xl, yl) = (120, 80)$, and the only restriction on chain length is $N \geq 4$ if not otherwise stated. The relative random error of the data is about 0.5% or better: (a) $4 \leq N \leq 200$; (b) $50 \leq N \leq 150$. [c,d] The chain narrowing procedure described by Olaj and Lantschbauer[8] has been used with $f = 0.05$ or 0.1, respectively. [e] The EP kinetic scheme has been used. [f] (160, 120). [g] (200, 180). [h] (120, 80, 2). [i] Relative random error is about 3%.

Table II
Rms End-to-End Distances and Gyration Radii
(Key as in Table I)

N	$\langle r^2 \rangle^{1/2}$	$\langle s^2 \rangle^{1/2}$	N	$\langle r^2 \rangle^{1/2}$	$\langle s^2 \rangle^{1/2}$
		$\langle N \rangle = 100^a$			
32	6.96	3.10	48	8.77	3.88
96	13.08	5.73	97	13.71	5.86
128	15.66	6.79	192	20.0	8.58
		$\langle N \rangle = 100^{a,e}$			
32	7.30	3.11	48	9.15	3.94
96	13.34	5.77	97	14.04	5.96
128	16.17	6.77	192	19.41	8.49
		$\langle N \rangle = 100^b$			
96	13.18	5.76	97	13.93	5.91
128	15.67	6.79			
		$\langle N \rangle = 100^c$			
96	13.25	5.78	97	13.91	5.90
128	15.75	6.81			
		$\langle N \rangle = 25$			
16	4.97	2.14	24	6.35	2.73
32	7.63	3.26	48	9.92	4.17
		$\langle N \rangle = 100$			
32	6.91	3.09	48	8.72	3.87
96	13.09	5.74	97	13.84	5.89
128	15.44	6.74	192	19.83	8.51
		$\langle N \rangle = 200^f$			
32	6.71	3.05	48	8.36	3.82
96	12.12	5.54	128	14.81	6.54
192	18.85	8.29	256	21.60	9.56
		$\langle N \rangle = 400^g$			
32	6.46	3.04	48	8.17	3.75
96	11.88	5.47	128	14.08	6.42
192	17.67	7.97	256	20.54	9.26
400	26.71	11.83	512	30.02	13.36

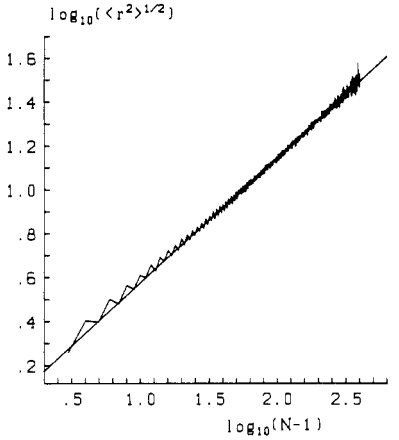

Figure 2. Rms end-to-end distances for the distribution in Figure 1a. The straight line is the best fit to the data, where each data point has been weighted according to its frequency. See Table I for the results of the fit. The small chains deviate slightly from the fitted line. If only chains from the interval $4 \leq N \leq 30$ are fitted, the exponent is 0.556, while the exponent determined from all data is 0.565.

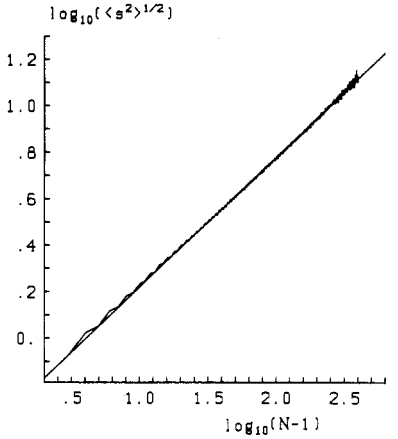

Figure 3. Rms gyration radii for the distribution in Figure 1a; see also Figure 2.

This oscillation is also observed for the isolated chain on the square lattice,[20] but it is much more dramatic in the melt. The simulations shown in Figure 1 were done with the natural kinetic scheme for end-segment reactions, which corresponds to a kinetic model where each end reaction, whether intramolecular or intermolecular, has equal probability. The oscillation seen in Figure 1a is probably not just a lattice effect but is enhanced by the kinetics, which is apparent from the fact that they are stronger in the more constrained case in Figure 1b than in Figure 1a. Chains with an even number of segments can, for instance, assume configurations where the end segments are neighbors. Chains in such a conformation participate less frequently in intermolecular reactions, where the chain length may change, than other chains. To a smaller extent, such an odd–even oscillation for chains on a square lattice has also been observed by Tuthill and Sui.[21] They used a related method, which had originally been introduced by Jaric and Bennemann,[22,23] to study equilibrium polymerization. It is curious that with our simulations the oscillation is observed even for fairly large chain lengths.

To see if we could suppress the oscillation, we used the equal probability or EP scheme as described above, where the probability of chain ends to react should be more equal and less dependent on neighbors and conformation. Even with this scheme, we still got a similar strong odd–even oscillation (not shown). Calculations in three dimensions exhibit an odd–even oscillation too (not shown) but much less pronounced than in two dimensions. Further, with the EP scheme the oscillation is smaller in amplitude than with the natural kinetic scheme; probably because of the high degree of interpenetration in three dimensions, almost every end segment has a neighbor suitable for an intermolecular reaction.

An oscillation between odd and even chains can be seen also for the rms end-to-end distances and the rms gyration radii, which are shown for the distribution in Figure 1a and in Figures 2 and 3. However, odd and even values are fairly symmetric around a central straight line to which they slowly converge. We used the tangent of the central straight line for the exponent of the scaling law. The dimensions of small chains scale with a slightly smaller exponent than the average-sized chain fraction; see, for instance, Figure 2, but we ignore this difference.

With the EP scheme we get slightly smaller exponents for the scaling of the end-to-end distance, Table I, than with the natural kinetic scheme, but this is due to the fact that the end-to-end distances of small chains are larger with the EP scheme, Table II. With the natural kinetic scheme we get a slightly larger exponent for the end-to-end distance than for the gyration radius, while for the EP scheme the opposite is true, which suggests that neither scheme yields strictly accurate results. The EP scheme probably violates the principle of detailed balance; i.e., backward and forward reactions between two given states are not equally probable. Although it is also not clear that the natural kinetic scheme yields the correct ensemble, we used it for most calculations.

If we subject the chain-length distribution to a stronger constraint than in the simulation shown in Figure 1b, we get slightly different results. We either forced the chain lengths into a symmetric interval, $0.5\langle N\rangle \leq N \leq 1.5\langle N\rangle$, where the distribution assumes its maxima near the ends of the interval (not shown) while in three dimensions the distribution with such a constraint is almost rectangular,[19] or forced it to be narrowly distributed around the average value as done by Olaj and Lantschbauer[8] in three dimensions. The Olaj–Lantschbauer method is fast and convenient, but it does not yield a simple equilibrium distribution. However, if we use a Gaussian constraint instead, the results are very similar (not shown). With both constraints the exponents increase slightly, Table I, but the rms radii of gyration and end-to-end distances do not change very much, Table II, which is also apparent from the fact that the preexponential factors become smaller than in the unconstrained case. With the usual screening argument one would expect that the exponent is smaller for a monodisperse melt than for a polydisperse melt. It is conceivable that the dense packing of monodisperse chains in two dimensions is more difficult to achieve than the dense packing of a polydisperse chain ensemble and that in two dimensions this effect may dominate the exponent when it is already close to $^1/_2$. However, if the chain-length distribution is forced to be very narrow, only few pseudokinetic rearrangements are possible and the simulation converges slower. With the constraint $0.5\langle N\rangle \leq N \leq 1.5\langle N\rangle$ about $^1/_3$ of the attempted intermolecular rearrangements are successful and with the Olaj–Lantschbauer constraint and $f = 0.05$ the success rate is about $^1/_5$ for $\langle N\rangle = 100$. However, probably more severe is the fact that with narrow constraints locally some configurations may be very stable. In Figure 4 we show a typical snapshot of the melt simulated with almost no constraint on chain lengths to illustrate chain conformations and neighbors of chain ends. It is clear that some chain ends will remain stable if narrow constraints are

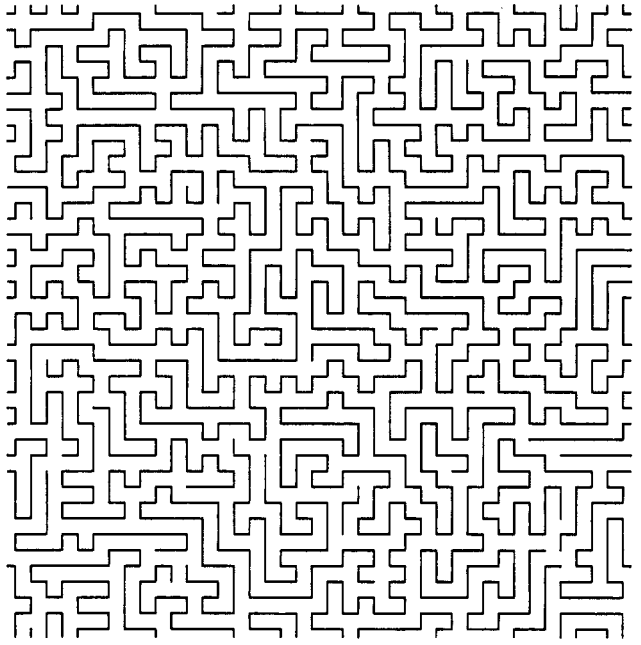

Figure 4. Melt for the distribution corresponding to Figure 1a is shown but which is simulated on a (40, 40) lattice to give a better magnifaction for viewing. The scaling results are the same as with the bigger lattice. The extensions at the lattice boundaries, which have half the length of a bond, are connected to the extensions at the other side of the lattice (periodic boundary conditions).

used. However, the stability of local structures is difficult to predict because it depends on many local reactions. The melts simulated with the constraints described above are indistinguishable by eye from Figure 4 except for the occurrence of small chains in the latter. The safest conclusion is that the bond-breaking method should be used with caution in two dimensions when a narrow constraint on chain distribution is employed.

The most reliable results are probably those obtained with almost no constraints on the chain-length distribution. It is seen from Table I that for these simulations the scaling exponents are about 0.54–0.55 for the melt with the longest average chain length studied and the exponents and the chain dimensions decrease with increasing average chain length. Since in a dense melt the distances between the centers of mass of different chains increases with chain length as $N^{1/d}$, in three dimensions even at short chain lengths a given chain is in contact with very many different chains. However, in two dimensions, if the chain dimensions would scale with exponent $^1/_2$, a given chain would be in contact with a constant number of chains. Therefore, from this simple argument alone,[3] one would expect for any finite chain length that chain dimensions scale with an exponent of slightly larger than $^1/_2$ in two dimensions and that the asymptotic exponent, whether it is $^1/_2$ or slightly larger, is reached only at very long chain lengths.

As mentioned in the introduction, Baumgärtner[14] and Carmesin and Kremer[15] investigated two-dimensional melts at volume fractions smaller than unity. Baumgärtner used the slithering snake method at a volume fraction of $^5/_6$ and for chain lengths up to 59 and found that the chain dimensions scale with an exponent of $^1/_2$. He also gave a relation for the rms end-to-end distance, $\langle r^2\rangle^{1/2} = 1.45(N - 1)^{1/2}$, $N > 30$. The rms end-to-end distances for $N = 48$ and $N = 96$ calculate as 9.94 and 14.13, respectively. Since he worked at a volume fraction smaller than unity, his chains are more swollen than ours, Table II. Carmesin and Kremer used the bond fluctuation method for chain lengths up to 100 and volume fractions from 0.4 to 0.8. They also found an exponent of about $^1/_2$.

We did also simulations on a two-dimensional layer with a thickness of two segments in the z direction and hard walls at the z boundaries. In the thicker layer the exponents, which are calculated from the x and y dimensions, are slightly larger than in the quadratic lattice and hardly change with narrower constraints on the chain-length distribution, Tables I and II.

The lattice dimensions xl and yl were chosen unequal to check whether the periodic boundary conditions had any influence on the results, but no significant difference between the x and y directions has been observed; see also the exponents for $\langle N\rangle = 100$ in Table I.

Conclusions

Chains in a dense two-dimensional athermal melt scale with an exponent for the rms end-to-end distance and the rms gyration radius of about 0.54–0.55 for an average chain length of 400 if simulated with the bond-breaking method on a quadratic lattice and with no or moderate constraints on the chain lengths. This exponent and also the dimensions of the chains at a given chain length seem to decrease further with increasing average chain length. The chain length distribution obtained in the simulations is qualitatively similar to the most probable distribution. In three dimensions the scaling results do not change with narrowing the distribution, but in two dimensions we get slightly increasing exponents with narrower chain distributions, which is most probably an artifact of the simulation method.

The value 0.54–0.55 is an upper bound for the asymptotic scaling exponent because as stated it seems to decrease with increasing average chain length. Monte Carlo studies[14,15] with the slithering snake method and the bond fluctuation method on monodisperse two-dimensional melts at volume fractions smaller than unity suggest that chain dimensions scale with an exponent of $^1/_2$ already for chain lengths smaller than 100. Our exponent is larger either because we have simulated a polydisperse melt or, maybe, because in a dense melt on a quadratic lattice due to packing constraints the scaling is sightly different than at lower volume fractions.

The scaling properties of polymer melts on a two-dimensional layer with a thickness of two segments in the z direction and with hard walls at the z boundaries are found to be similar to the scaling properties of polymer melts on the quadratic lattice.

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A Kinetic Theory of Stepwise Cross-Linking Polymerization with Substitution Effect

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ABSTRACT: A kinetic model describing evolution of the molecular size distribution during stepwise homopolymerization of a trifunctional monomer reacting with substitution effect is presented. The model makes use of a Smoluchowski-like coagulation equation. It is shown that the pre-gel molecular size distribution in kinetically controlled polymerizations differs from that generated by the cascade theory (or any other equivalent statistical theory) except for the systems with equal and conversion independent reactivities of functional groups.

1. Introduction

In 1982, Mikeš and Dušek[1] published results of a Monte Carlo study on the network formation by stepwise homopolymerization of a trifunctional monomer.

In fact, their study aimed at showing that, in kinetically controlled stepwise polymerization, the size distribution of polymer molecules differs from that generated by the acknowledged statistical theories of Flory,[2] Stockmayer,[3] Gordon,[4] and others[5,6] except for the special case of the so-called *random* polymerization. In the random polymerization, all functional groups have equal and conversion-independent reactivities.

Mikeš and Dušek considered several *nonrandom* cases where the so-called *first-shell substitution effect* (FSSE)[7,8] was operative. With FSSE, a monomer has all its f functional groups equally reactive until one of the groups reacts. Then the remaining $f - 1$ groups become again equally reactive, but with different reactivity. The same applies to the $f - 2$ groups in a doubly connected unit, etc. Hence, the FSSE models the conversion dependence of reactivity of functional groups that is quite common in real polymerization processes.

This work deals with exactly the same system as considered by Mikeš and Dušek except that their Monte Carlo approach is replaced by a more straightforward analysis of the distribution of polymerization degrees. The techniques used in this work are very similar to those published by Kuchanov and Povolotskaya.[9,10] The analysis is based on a kinetic equation of the Smoluchowski type.[11] This equation (rederived in the Appendix section) is used to calculate various averages of the degree of polymerization as well as the time and conversion degree at the gel point for a number of nonrandom model systems of homopolymerization of a trifunctional monomer.

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2. Statistical versus Kinetic Theory of Cross-Linking Polymerization with Substitution Effect

The following polymerization process is considered. At time $t = 0$, the system of constant volume contains $N \to \infty$ units, each having three functional groups. The groups of different units react *irreversibly* with each other to form bonds. No intramolecular reactions are allowed. The units with i reacted groups are referred to as i state.

While considering the FSSE, it is reasonable to assume additivity of activation energies.[7] Thus, the activation energy of reaction between two units (with i and j functional groups already reacted) is taken to be

$$\Delta E_{ij} = \Delta E^* + \psi(i) + \psi(j) \tag{1}$$

where ΔE^* is the activation energy for the reaction of functional groups in a reference state and $\psi(\cdot)$ is the contribution of the unit substitution degree to the activation energy of reaction of its groups.

In terms of rate constants, eq 1 is equivalent to

$$K_{ij} = K^* K_i K_j \tag{2}$$

so that the effects of substitution upon the reactivity of groups in two reacting units are separable.

The set of elementary reactions between units in homopolymerization of a trifunctional monomer is shown in Figure 1.

This set can be analyzed in two ways: by using a statistical or kinetic method.

A convenient statistical approach is the one developed by Gordon and Scantlebury.[7] In this approach, the distribution of molecular sizes is generated from the distribution of units by states. Thus, the fractions, α_i, of units with i reacted groups are calculated from the set of differential equations

$$-\mathrm{d}\alpha_i/K^*\,\mathrm{d}t = [(3-i)K_i\alpha_i - (3-i+1)K_{i-1}\alpha_{i-1}]\sum_{j=0}^{2}(3-j)K_j\alpha_j \qquad i = 0, 1, \ldots, 3; \quad \alpha_{-1} \equiv 0 \tag{3}$$

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