Macromolecules **2002,** *35,* 8239−8242

Notes

On the Reshuffling of Polymer Segments in Star Polymer Systems

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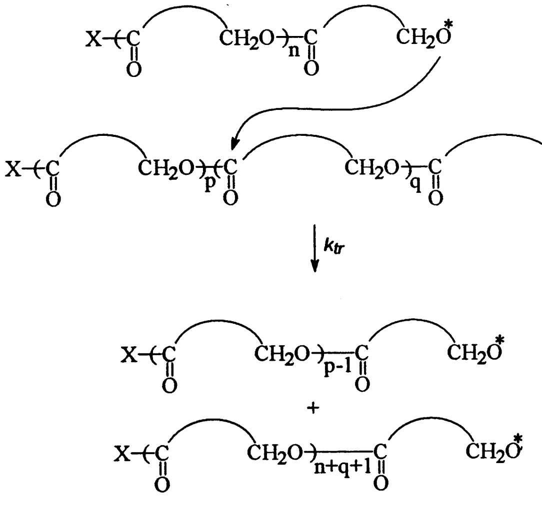
Received March 28, 2002
Revised Manuscript Received July 3, 2002

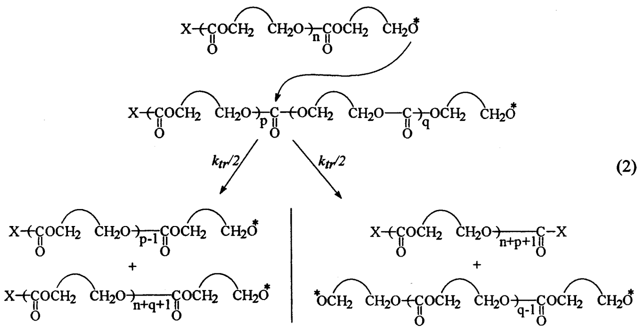
Introduction

Star polymers are often prepared by polymerization initiated with multifunctional initiators. If the ring opening polymerization (ROP) process is used, then one has often to consider the reshuffling reactions leading to segmental exchange of growing macromolecules. However, depending on monomer structure, there are two possibilities—chain scission can occur unidirectionally, as for instance in polymerization of lactones,[1] lactams,[2] etc. or bidirectionally (two directions of chain cleavage are equally probable), as for instance in polymerization of cyclic carbonates,[3] acetals,[4] ethers (cationic process),[5] sulfides,[6] phosphoric esters,[7] etc.



(1)

Although the dependence between the polydispersity index of star polymer arm and the overall polydispersity index of star polymer formed by coupling of linear chains with multifunctional coupling agent is well-known,[8,9] most of authors preparing star polymers did not take into account this relationship while discussing the observed polydispersity index.



The equation relating $\mathrm{PDI}_{\mathrm{star}}$ with $\mathrm{PDI}_{\mathrm{arm}}$, modified by taking into account the molecular weight of the star core, is the following:

$$\mathrm{PDI}_{\mathrm{star}} = 1 + \frac{\mathrm{PDI}_{\mathrm{arm}} - 1}{f}\cdot\left(\frac{\bar{M}_{\mathrm{n(star)}} - M_{\mathrm{core}}}{\bar{M}_{\mathrm{n(star)}}}\right)^2 \qquad (3)$$

(derivation is presented in the Supporting Information), where $\mathrm{PDI}_{\mathrm{arm}}$ is the PDI of arms of star polymer, f is the number of arms in a star macromolecule, $\bar{M}_{\mathrm{n(star)}}$ is the number average molecular weight of star polymer, and M_{core} is the molecular weight of a star core.

If coupling is not complete, the following equation results:

$$\mathrm{PDI}_{\mathrm{star}} = 1 + \frac{\mathrm{PDI}_{\mathrm{arm}} - 1 + p_0}{f(1 - p_0)}\left(\frac{\bar{M}_{\mathrm{n(star)}} - M_{\mathrm{core}}}{\bar{M}_{\mathrm{n(star)}}}\right)^2 \qquad (4)$$

Here p_0 is the probability that a coupling site did not react, equal to the fraction of unreacted coupling sites.

In fact, eq 3 (and in some cases eq 4) can be applied as well to star polymers formed by initiation of polymerization with multifunctional initiators, provided initiation with all initiator functions is fast. However, as the discussed equation does not take into account different polydispersity indexes of star arms formed at different monomer conversions, it cannot be applied to systems with slow initiation.

It is especially important to perform the corresponding computation of the average PDI of star arms for ring opening polymerization systems with reshuffling process possible.

For instance, it is often claimed (e.g., refs 10−12) that the resulting star polymer has narrow molecular weight distribution (MWD), while, in fact, computing (according to the rearranged eq 3) the $\mathrm{PDI}_{\mathrm{arm}}$ gives a value close to 2, characteristic for the most probable distribution. This result, if obtained for systems with reshuffling, means that the polydispersity index of a star polymer is in fact the highest possible, provided there are no additional reactions changing a macromolecule topology and initiation is fast.

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10.1021/ma0204958 CCC: $22.00

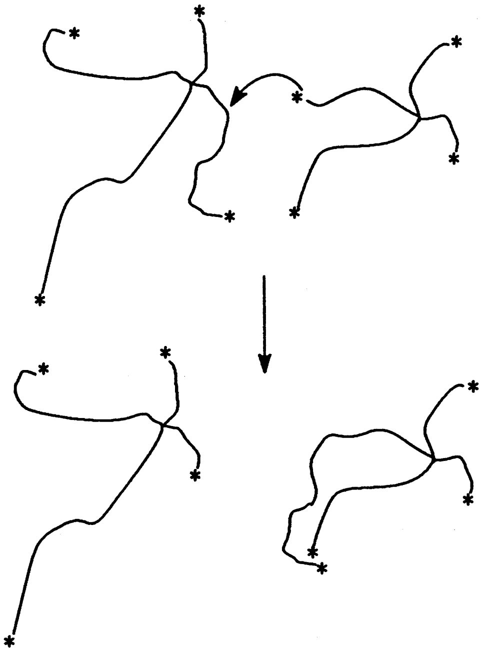
If all the above-mentioned complications are absent, then according to eq 3 the equilibrated (because of the reshuffling processes) polymer with the most probable distribution of the arm lengths has PDI much lower than 2. Depending on the number of star arms (in parentheses) the PDI values are the following: 1.333 (3), 1.250 (4), 1.200 (5), and so on (M_{core} is considered to be negligible).

The present paper shows results of the Monte Carlo simulations of the evolution of the MWD in polymerization systems initiated with multifunctional initiators. To simplify computations, instantaneous initiation with all initiator functions was assumed. In other words, the starting molecule in simulations was starlike living n-mer, containing n active centers at unit-length arms.

The paper is the third one in a series on modeling of segmental exchange in polymerization systems and the same general method of computation was applied as previously,[13,14] modified correspondingly. As presented in this paper, Monte Carlo simulations of the analyzed polymerization systems have proved that there is a simple way, without simulations, to estimate evolution of the MWD in systems with unidirectional chain scission, provided kinetic parameters are known. In bidirectional chain scission systems one can predict the MWD more precisely using Monte Carlo computations.

Results and Discussion

Unidirectional Chain Scission Systems. When only unidirectional chain scission is possible, reshuffling processes do not change topology but only lengths of arms of the star macromolecules (polylactones, polyamides, etc.):



(5)

Results of the Monte Carlo simulations are shown in Figure 1 presenting the MWD curves (SEC resembling representation) computed for several degrees of monomer conversion and four types of initiator: mono-, di-, tri-, and tetrafunctional. The frequency and weight distribution curves computed for the same systems are available as Supporting Information. Relative concentrations of monomer and active species were chosen to be equal in all cases. Consequently, DP_n of arms in different star (and linear) polymers were equal at the same monomer conversions, but the overall DP_n differed.

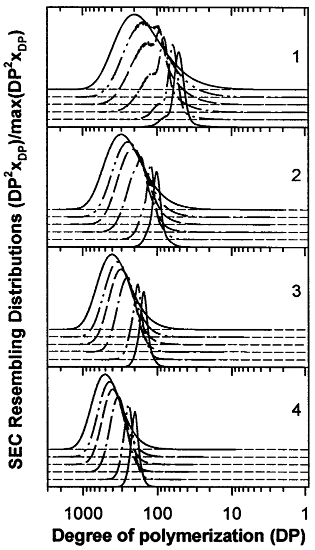


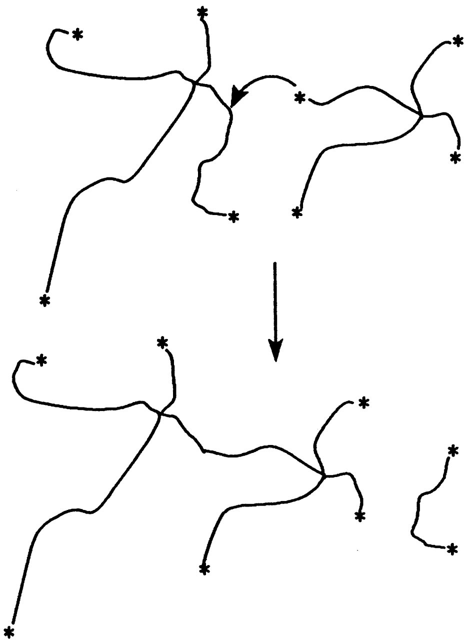
Figure 1. SEC resembling representation of MWD obtained by Monte Carlo simulations of reshuffling in polymerization initiated with monofunctional (1), difunctional (2), trifunctional (3), and tetrafunctional (4) initiators. $[M]_0/([I_f]_0 f) = 100$ (f = initiator functionality), $k_p/k_{tr} = 100$. Only unidirectional chain scission possible. Monomer conversions from down to up: 0.50, 0.60, 0.80, 0.90, 1.00. DP_n and PDI values, computed correspondingly: (1) 50.0, 1.085; 60.0, 1.127; 80.0, 1.308; 90.0, 1.508; 100.0, 1.990; (2) 100.0, 1.042; 120.0, 1.063; 160.0, 1.154; 180.0, 1.254; 200.0, 1.495; (3) 150.0, 1.028; 180.0, 1.042; 240.0, 1.103; 270.0, 1.170; 300.0, 1.330; (4) 200.0, 1.021; 240.0, 1.032; 320.0, 1.077; 360.0, 1.128; 400.0, 1.248.

The polydispersity indexes are noted in a caption to Figure 1. One can see that the higher functionality of initiator gives a narrower MWD, so the dependence is exactly as expected from eq 3.

Bimodal distributions can be observed only for monofunctional initiators where two populations of polymer chains, namely affected and not affected by reshuffling, differ by their MWD but DP_n. Although difunctional initiators give linear macromolecules as well, the segmental exchange reactions do not lead in these systems to bimodal MWD, similarly as for star polymers. It is so because in these systems there are more than two, namely three, different populations of macromolecules (with zero, one, and two arms affected by reshuffling), and their MWD functions overlap hiding multimodality, similar to star polymer systems, where one can distinguish a higher number of macromolecule populations.

Results conforming eq 3 prove that the presented in the first paper[13] from the series a method of prediction of PDI in polymerization systems with reshuffling of polymer units on the basis of known kinetic parameters of polymerization system can be applied to systems with multifunctional initiators, similar to the way it could be done for linear systems,[15,16] provided no disproportionation of macromolecule functionalities occurs. According to the described in the cited paper method, one can predict PDI of arms in star polymers. Then, applying eq 3. the PDI of the star polymer can be computed. In a manner similar to that used for linear systems, the method can also be applied to estimation of k_p/k_{tr} on the basis of the experimental data of PDI of star polymers vs monomer conversion. It can be done can in a simple way, not performing any curve fitting computations. At first, one has to use the rearranged eq 3 to compute PDI$_{arm}$, then, using nomograms or equations given in the cited paper,[13] can get the value of k_p/k_{tr}. More accurate results can be obtained by the curve fitting of SEC data to the simulated chromatograms, similar to those shown in Figure 1.

Bidirectional Chain Scission Systems. When bidirectional chain scission is possible then the reshuffling processes change not only the lengths of arms of the star macromolecules but also topology and functionality of macromolecules as well (polycarbonates, polyphosphates, polyethers in cationic systems, disulfides, etc.):



(6)

Consequently, linear difunctional chains are formed as well as various types of branched and hyperbranched macromolecules. It is so because the first products with two branching points can react between themselves, and the next products continue the exchange processes.

Monte Carlo simulations shown in Figure 2 (SEC resembling MWD curves) and in the Supporting Information (frequency and weight distribution plots) indicate that reshuffling processes lead to extremely inhomogeneous product with very high PDI for higher functionality initiators. The final PDI is the higher the higher the initiator functionality is.

Multimodal MWD plots are observed. Separate peaks correspond to macromolecules differing in a number of branching points.

The breadth of MWD is the larger, the higher the degree of disproportionation of macromolecule functionalities is, i.e., the lower fraction of monofunctional elementary chains (connecting an initiator residue—a star core or a branching point when initiator functionality (f) is higher than 2—with an active center). The other types of elementary chains are difunctional ones, linear with both active ends, and zerofunctional ones, polymer fragments connecting two initiator residues (branching points when $f > 2$). The higher is the degree of disproportionation the higher fraction of difunctional and zerofunctional elementary chains (separate linear difunctional chains and ones connecting two branching points, respectively) and the higher structural inhomogeneity of the polymer.

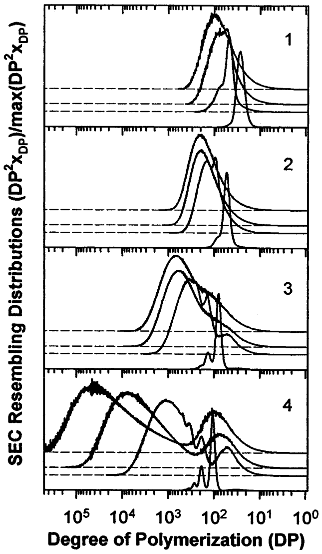


Figure 2. SEC resembling representation of MWD obtained by Monte Carlo simulations of reshuffling in polymerization initiated with monofunctional (1), difunctional (2), trifunctional (3) and tetrafunctional (4) initiators. $[M]_0/([I_f]_0 f) = 100$ (f = initiator functionality), $k_p/k_{tr} = 100$. Bidirectional chain scission is possible. Monomer conversions and corresponding fractions of monofunctional (connecting initiator residue with active center) elementary chains, for each of boxes from down to up: 0.52, 0.912; 0.90, 0.631; 0.988, 0.545; 0.996, 0.519. DP$_n$ and PDI values computed correspondingly: (1) 26.0, 1.085; 45.5, 1.308; 45.5, 1.508; 49.8, 1.990; (2) 52.0, 1.088; 90.1, 1.499; 98.8, 1.835; 99.6, 1.917; (3) 78.0, 1.168; 135.2, 2.489; 148.3, 3.880; 149.5, 4.273; (4) 104.0, 1.276; 180.2, 6.323; 197.7, 36.65; 199.3, 180.5.

However, one has to remember that simulations were performed with an assumption that no cyclization reactions operate in the studied systems. In fact, cyclizations are inevitable, and therefore, the resulting PDI values are overestimated. The role of cyclization in PDI of hyperbranched polymers was studied, for instance, by Dusek et al.[17] Nevertheless, formation of an inhomogeneous polymer is indisputable. One can expect even gel formation, which in fact was observed in some systems.[12] The higher the number of arms, the lower the reshuffling degree at which inhomogeneity can clearly be observed is.

Conclusions

Monte Carlo simulations appeared to be a good tool for analysis of reshuffling processes in polymerization systems with multifunctional initiators.

PDI in systems without disproportionation is lower than in analogous monofunctional initiator systems. A method of prediction of PDI in such systems was proposed. It is also possible to determine k_p/k_{tr} in these systems on the basis of the experimental dependence of PDI on monomer conversion.

In systems with bidirectional chain scission possible, disproportionation of chain functionalities leads to inhomogeneous polymer, with broad MWD, containing, beside star structures, linear difunctional chains and multibranched macromolecules.

Inhomogeneity appears at the lower degree of reshuffling the higher number of arms in starting star macromolecules. Extremely high PDI values of resulting polymer can be expected.

Computations

Monte Carlo simulations were performed using a method described in the previous papers,[13,14] modified by introducing a procedure of building a composite macromolecule composed of elemental chains (monofunctional in systems without disproportionation and additionally of mono and zerofunctional in systems with disproportionation).

An assumption of instantaneous initiation was adopted. Consequently, starting macromolecules were star structures with all arms of one unit length.

Acknowledgment. The work was financially supported by a grant of the State Committee of Scientific Research (KBN, Poland), No. 3 T09A 003 17.

Supporting Information Available: Text giving the derivation of eqs 3 and 4, and figures presenting frequency and weight distributions of polymers from Figures 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0204958