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Gelation in the non-stoichiometric step growth polymerization of two- and three-functional monomers

RAPID COMMUNICATION

Summary — A random step grow polymerization of two-functional (A_2) and three-functional (B_3) monomers was studied using a computer simulation method. The focus was on the effect of dividing the process into stages onto the weight-average polymerization degree (P_w) of the resulting polymeric product. It was found that by applying the procedure one can bring to gelation a system that does not form a network when polymerized in a single stage. Such an effect known previously as a result of changes in stoichiometry of a system, can also be observed when the ratio of monomers is the same throughout the whole process. Then, the gelation stems from the growth history of macromolecules.

Key words: step growth polymerization, two-functional monomer, three-functional monomer, gelation, polymer networks, Monte Carlo simulation.

ŻELOWANIE W PROCESIE NIESTECHIOMETRYCZNEJ POLIMERYZACJI STOPNIOWEJ MONOMERÓW DWU- I TRÓJFUNKCYJNYCH

Streszczenie — Metodami symulacyjnym badano przebieg polimeryzacji stopniowej monomeru dwufunkcyjnego (A_2) z monomerem trójfunkcyjnym (B_3). Określano jaki wpływ na wagowo-średni stopień polimeryzacji układu (P_w) ma dzielenie procesu polimeryzacji na etapy. Stwierdzono, że dzięki etapowemu prowadzeniu polimeryzacji można uzyskać żelowanie układu, podczas gdy w procesie jednoetapowym nie zauważa się tendencji do tworzenia sieci polimerowej. Efekt taki, obserwowany wcześniej w procesach przebiegających ze zmianą składu stechiometrycznego podczas procesu, może zatem występować także w układach o stałym podczas całego procesu wzajemnym stosunku ilościowym substratów. W tym przypadku żelowanie układu wynika z historii wzrostu makrocząsteczek.

Słowa kluczowe: polimeryzacja stopniowa, monomer dwufunkcyjny, monomer trójfunkcyjny, żelowanie, sieci polimerowe, symulacja Monte Carlo.

A full statistical analysis of network formation in a copolymerization of two-functional (A_2) and three-functional (B_3) monomers, each with identical functional groups A or B reacting with each other, was provided over half a century ago by Flory [1]. Flory calculated the critical conversion at gelation for both stoichiometric and non-stoichiometric mixtures of monomers. Whether a polymerization system involving multifunctional monomers does gelate or not depends, beside of the ratio of monomer concentrations, also on the reactivity of functional groups, including the so called substitution effect, *i.e.* the change of reactivity of initially identical groups, after one of them has reacted [2].

The non-stoichiometric polymerization of monomers A_2 and B_3 has recently became again an object of interest of both theoretical [3, 4] and experimental studies [5—8] as one of methods of preparing hyperbranched polymers. The composition and structure of the hyperbranched products prepared in this way depend not only on the monomer molar ratio and kinetic parameters, but also on the procedure of introducing monomers into the polymerization reactor [9, 10]. For example, a system that does not gel in a one batch polymerization can be forced to gel, when the excess monomer is divided into portions and introduced into polymerization reaction in several portions at predetermined conversion of previously present monomers [11]. This seemed understandable, as the system reacted from the start at the monomer ratio securing gelation and the excess of a monomer introduced at later stages of reaction could not postpone the gelation beyond the total conversion of minority groups. It turns out however, that a non-stoichiometric mixture of monomers A_2 and B_3, unable to gelate, if polymerized as one batch, can be forced to form infinite network, after all, again by dividing monomers into portions, but this time with each portion having the same monomer composition.

This is demonstrated in this report using Monte-Carlo simulation methods.

Simulation procedure

In the simulation of the polymerization process, *i.e.* performing the process in computer memory, the total number of monomer molecules A_2 and B_3 taken in a predetermined molar ratio was divided into several equal portions. The total number of monomer molecules used in all simulations was 1 000 000. The first portion was placed in the virtual reactor and the condensation reaction had been carried out until a predetermined degree of conversion was reached. Then the next portion of monomers was added, the molecular parameters were updated and the simulation continued. The conversion degree (p) of the minority functional groups (A or B) was the measure of reaction progress. Another conversion parameter, defined in the same way, was related to the conversion of groups so far introduced to the reactor. This parameter was denoted as p_A or p_B, depending on the type of minority groups. No substitution effects were taken into account.

RESULTS AND DISCUSSION

The changes in P_w value are shown in Fig. 1 as functions of conversion p in the random non-stoichiometric polymerization of monomers A_2 and B_3 with monomers introduced into the reactor in three portions. The molar ratio of monomers was A_2:B_3 = 2:3 (the stoichiometric ratio is 3:2 [1, 2]). Each curve represents the simulation differing in the moment of introducing the next monomer portion (p_A). The curve representing one batch (single step) polymerization (p_A = 0) is also shown for comparison.

The results indicate that as the moment of introducing the next portion of monomers was postponed (increasing p_A), the process could completely change its character. From the reaction yielding a relatively low molecular weight product at high conversion, one could obtain gel, *i.e.* the product with diverging P_w. Gelation is observed for the system where each next portion of monomer mixture is introduced after a little more than 70 % of previously introduced minority monomer (here A_2) has reacted. It is worth noticing that the P_w attainable in the system increases as the moment of introducing each next monomer portion is postponed. Hence, the change of procedures of carrying out the polymerization can be employed to increase the molecular weight of the product or even bring it to gelation.

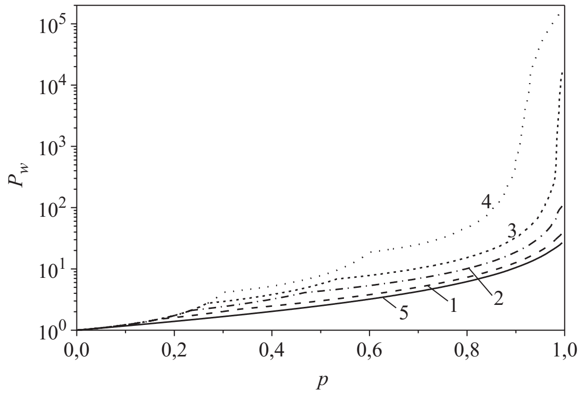

Fig. 1. Changes in the weight-average degree of polymerization (P_w) versus conversion degree of minority groups in the whole system (p) in the random step polymerization carried out in three stages with monomer ratio A_2:B_3 = 2:3 with each next portion of monomer introduced at p_A equal to: 1 — 0.5, 2 — 0.7, 3 — 0.8, 4 — 0.9, 5 — 0

Similar computer experiments were carried out earlier for non-stoichiometric systems with an excess of A_2 monomer (A_2:B_3 = 3:1), used in the ratio that does not lead to gelation in one batch reaction. In this case gelation for a three stage system was observed at relatively small value of p_B, about 0.3 [12].

This work shows that as the ways of dividing polymerization systems, particularly those non-stoichiometric ones, into different numbers of parts of equal or non-equal size, as well as a number of methods of introducing these parts into polymerization reactor open a wealth of methods of modifying the polymerization processes aimed at producing a tailor made polymer products.

CONCLUSIONS

A modification of a non-stoichiometric polymerization of monomers A_2 and B_3 consisting of dividing the polymerization into stages may in some cases dramatically change the process of polymerization and force an originally non-gelling system to undergo gelation. This dramatic change does not necessarily involve any change in stoichiometry of the system, but depends solely on the history of polymerization. As large branched molecules have a chance to be formed at the early stages of reaction, the system can gelate at the later stages since these large components, having high probability to react, grow much quicker than in the system with molecules growing at comparable rate.

The practical value of the observation is quite important as it may help to increase the molecular weight of some polymeric products. The method of introducing extra monomers at later stages of polymerizations has in fact been already in use in some industrial condensation processes, probably developed by the trial and error method.

The fact of occasional producing a gel in the condensation systems that is supposed to yield a hyperbranched polymer only, seems now easier to explain, since similar results as division of a system into portions may be generated by *e.g.* local overheating in a reactor, causing some reactants to reach higher conversion than in other parts of the reactor.

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