# **ՏԱՅԱՍՏԱՆԻ ՏԱՆՐԱՊԵՏՈԻԹՅԱՆ ԳԻՏՈԻԹՅՈԻՆՆԵՐԻ** ԱՉԳԱՅԻՆ ԱԿԱԴԵՄԻԱ НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF ARMENIA

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# ADVANTAGES OF THE METHOD OF FRONTAL POLYMERIZATION IN HIGH TECHNOLOGIES

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This paper is devoted to advantages and opportunities of frontal polymerization applied to nanotechnologies with the aim to obtain polymeric nanocomposites with a uniform distribution of nanoparticles in polymer matrix. It can also be used in the synthesis of high temperature superconducting polymer ceramic intercalated composites and superconducting electrically conductive polymer composites.

It has been shown that the frontal polymerization allows obtaining multifunctional, gradient materials due to the specificity of the propagation process of heat wave polymerization.

The frontal polymerization has a significant contribution to the synthesis of pure super absorbent hydrogels, in contrast to traditionally obtained, and many others.

Figs. 7, references 24.

# Introduction

For a better assessment of the advantages of frontal polymerization, we would like to present a small comparison of exothermic radical polymerization in traditional technologies with frontal polymerization (FP), occurring in the mode of auto-wave propagation of thermal polymerization.

In the traditional methods after initial mixture is loaded into the reactor, it is heated to the temperature at which initiator decomposes to yield active radicals. From this moment, exothermic polymerization takes place with the formation of high-molecular polymer chains. A sufficiently large amount of heat is released. In order to avoid thermal explosion in the industry, cooling systems are installed around the reactor. To reduce the polymerization rate, respectively, to reduce the rate of released heat, inert solvents are often added to the initial mixture. At the end of the process, solvents are either released into the atmosphere polluting the environment or cleaned and reused (which complicates the process and makes it more expensive). It is one problem. From the point of view of non-isothermal processes in traditional technologies, there is also a problem. The fact is that large-size products are generally produced with internal defects - during the process of solidification into the sample defects are formed [1,2]. Therefore, we began to study the reasons and opportunities to avoid defects and create a controlled production of these products. These studies led to the idea of FP. This was in the seventies of the last century. At that time, only our laboratory in the branch of the Moscow Institute of Physical Chemistry, in Chernogolovka, was engaged in the FP method; and up to the 90s we were the only ones engaged in the FP–monopoly [3–8].

## **Experiment and discussion**

Fig. 1 shows a schematic polymerization in the conditions of FP [1]. The reaction ampoule is loaded with the initial mixture; the heat is supplied not to the entire reactive mass. In the FP method the process is carried out by local and short warm-up of the local part of the reactor (for example, one end of the tubular reactor) filled with the reacting mixture. The polymerization process is initiated at the site of heating. The heat evolved is transferred to the neighboring layer of unreacted reaction mixture. In this layer a new round of polymerization is initiated followed by the corresponding release of heat to warm the neighboring layer, and thus the polymerization process extends from one end of the reactor to another in the autowave mode. This process fixes properties of the composite, which are determined by the initial mixture.



Fig. 1. Schematic polymerization in the conditions of the FP method

Unlike the traditional methods of synthesis, here we are interested in preserving this heat, so that it does not leave the walls of the reactor, but transfers to an adjacent layer. In FP it is necessary to keep the released heat, which is the initiator of the process and eliminates the need for heat removal, respectively, the use of solvents to reduce heat generation. This is the basis for the high productivity of FP and its environmental safety. Currently FP is the most researched subject in the world Scientist Centers and Universities, because of its rationality [9–14].

Therefore, until recently the FP was considered as a high-performance technological method, but with the development of high technologies, it became clear that this method was indispensable in the synthesis of polymer superconducting composites, moreover it has serious advantages in the synthesis of polymeric nanocomposites with a uniform distribution of nanoparticles in the polymer matrix [15–18].

It is known that to obtain polymeric nanocomposites filled with nanoparticles, different methods of passivation (neutralization of high activity of nanoparticles) are used. These include plasma polymerization, polymerization under conditions of acoustic waves, the use of surface-active materials (SAMs) and others.

All these methods are designed to protect the nanoscale of the added nanoparticles. The fact is that due to high activity, nanoparticles are attracted to each other and stick together, losing their nano-scale properties.

Acoustic waves prevent the nanoparticles from sticking together in the melt or solution of the polymerizable monomer. SAMs envelop a nanoparticle with the formed micellar single-charged structures and thereby make the nanoparticles passive, preventing them from sticking together. However, a serious problem arises here. A strong surfactant reacts with a nanoparticle, neutralizing its activity and attractiveness of nanoscale. Weak surfactants during the polymerization depart from the surface of the particles and stick together.

We have performed a series of experiments with the addition of surfactanttreated nanoparticles to the monomeric medium by the FP method. We did the same without processing nanoparticles in different thermal regimes. Below are presented the microscopic photographs of the samples obtained in the adiabatic, isothermal and frontal regimes. You can see that by FP, the initial state is fixed; in this case the uniform distribution of nanoparticles in the polymer matrix takes place. Two factors work here: the effect of the auto-wave propagation of the polymerization, analogous to acoustic waves and fast fixation of the initial state, which does not allow the particles to agglomerate.



Fig. 2. (a) Initial reaction medium without surfactant, (b) in the presence of surfactant, and (c) at 30X magnification of the microscope. Surfactant-treated, untreated surfactants.

This Figure shows microscopic photographs of a solution of acrylamide complex with nanoparticles additives.



Fig. 3. Effect of the thermal mode of polymerization on the structure of nanocomposites based on PAAM: (a) adiabatic mode, (b) frontal stationary mode, and (c) frontal oscillating mode.



Fig. 4. The micrograph of polymer-ceramic nanocomposites with the UHMWPE binder.

We note one more advantage of the FP for the synthesis of superconducting nanocomposites [19-24].

With the use of superconducting yttrium and bismuth ceramics as additives in the polymerizing system in order to obtain superconducting polymer composites, we succeeded in synthesizing HTSC composites with the 95-97 K transition by the FP method. As it turned out, this possibility was associated with the intercalation of polymer molecules into nanoscale interlayer spaces of ceramics. As can be seen from Fig. 4 due to the shock wave, high-molecular chains are introduced into nanosized ceramic layers (intercalation).



Fig. 5. Temperature profiles of stationary FP (AAm, Na acrylate, potassium persulfate).

As it is shown, the mode of FP is a process taking place in non-isothermal conditions of thermal propagation of the polymerization wave. It should be noted that along with significant advantages, there is a problem in the implementation of FP. Since every time with the change of the initial composition, the patterns on establishing stationarity change dramatically, in each particular case modeling, calculation of kinetic regularities are necessary, otherwise the technology cannot be implemented.

The propagation of the polymerization wave depending on the initial conditions, the kinetics and macro kinetics of the process must be stationary; as can be noted, in Fig. 5 the wave is stable and stationary; at any point the amplitude of the wave is stable. This is a linear, stable propagation of the polymerization wave. One of the most important conditions for stability is to ensure the flow of the process under conditions when there is no loss of heat to the environment.

Transition of the process from a linear stable state to an unstable (non-linear) state can lead to both a decrease in the non-uniform flow of the process and a decrease in the rate of proliferation, attenuation, and the formation of different spin regimes. Naturally, the properties of the resulting products will not meet the requirements, and the process may stop, or splash out of the reaction vessel.

Therefore, detailed study of kinetic and macro-kinetic models in the FP is necessary. Otherwise, all the advantages of the FP will be leveled by the instability of the process.

Having the appropriate data for the synthesis of various polymer and nanopolymer composites, we have the possibility of obtaining gradient polymeric samples. For example, if we have calculated methods for the synthesis of various composites including superconducting, electrically conductive composites, we can combine them in one sample and using the FP method obtain the corresponding gradient material with the required properties.



Fig. 6. A sample with gradient properties obtained by the FP method.



Fig.7. Schematic diagram of a film with (1) superconducting and (2) current-conducting properties obtained with the (1) UHMWPE and (2) AAM–MMA copolymer binder.

Fig. 6 exemplifies gradient polymeric material obtained by FP with sequentially arranged Co- and Ni-containing metal-complex monomers and AAM in which the chemical composition varies along the sample length. Here in the center we have a polymer composite with superconducting properties, obtained using the Cu complexes of acrylamide monomer with additives of superconducting ceramics, the next layer is complected with the Mn-acrylamide complexes with additives of nanosilver, due to which the resulting polymer composite acquires current-carrying properties.

When we interlace all these monomers, we require the desired gradient properties in advance. Such a sample cannot be obtained by traditional methods, since in the traditional process of polymerization the reagents are mixed in the volume of the reaction vessel and it is impossible to obtain material with different properties along the tube or radius. Fig. 6 and 7 show the appropriate starting alternating initial reagents in the reaction ampoule, and the conditions for the polymerization process are set in advance for the implementation of the stationary reaction front. Then the FP will lead to the creation of a multifunctional gradient sample according to the form as required along the length or along the radius of sample.

It is well known that functionally gradient materials (FGMs) with gradual (polyfunctional) properties have a wide range of applications and are claimed in various areas of national economy and techniques. Polymer nanocomposites with gradient properties suggested by our research group possess a wide range of sensitivity due to the combination of different properties in one particular pattern. Such a gradient multifunctional sample is a microchip appropriate for all kinds of devices, which need gradient properties in a one general pattern: chips for superfast calorimeters, for medical and biological analyses and so on. In this way, we can perform FGMs along the length and along the radius of the obtained polymeric materials.

For obtaining gradient polymeric materials by a traditional technology (where properties along the length of a tube or radius of a tube vary according to requirements) it is necessary to obtain separately the materials with required different properties, then to combine them in one sample with alternation of properties either in a direction of a tube radius or in a direction of length of the tube. Auto wave process of frontal polymerization fixes set gradient properties in one sample according to in advance set distribution of an initial mix either along a tube or along a radius.

### Conclusion

The article shows the frontal method, which is due to its specificity widely demanded in various fields of synthesis of polymers and polymer composites, as well as in high technologies, such as the synthesis of polymer nanocomposites, high-temperature superconducting interval composites, the gradient multifunctional composites in one polymerization stage. Thus, FP proved to be a unique method.

### ՖՐՈՆՏԱԼ ՊՈԼԻՄԵՐԱՑՄԱՆ ՆՎԱՃՈւՄՆԵՐԸ ԲԱՐՁՐ ՏԵԽՆՈԼՈԳԻԱՆԵՐՈԻՄ

#### Ա. Ղ. ՏՈՆՈՅԱՆ և Ս. Պ. ԴԱՎԹՅԱՆ

Ֆրոնտալ պոլիմերացման մեԹոդը, ի սկզբանե, գիտական ՀասարակուԹյան կողմից ընդունվում էր Հիմնականում որպես պոլիմերների և պոլիմերային կոմպոզիտների սին-Թեգի բարձր արտադրողականուԹյամբ և էկոլոգիապես անվտանգ մեԹոդ: Սակայն վերջին տասնամյակներում պարզվեց, որ չնորՀիվ ֆրոնտալ պոլիմերացման առանձնաՀատկուԹյանը, մեԹոդի կիրառումը բերում է զգալի նվաճումների բարձր տեխնոլոգիաների ասպարեզում` պոլիմերային նանոկոմպոզիտների, բարձրջերմաստիճանային ինտերկալացված պոլիմերային գերՀաղորդիչների, բազմաֆունկցիոնալ գրադիենտային պոլիմերային նյուԹերի սինԹեզի և այլ բնագավառներում: Ներկայացված ակնարկային Հոդվածում նկարագրված են Հեղինակների կողմից ստացված արդյունքները և միջազգային տվյալները` վերը Թվարկված խնդիրների վերաբերյալ:

### ПРЕИМУЩЕСТВА МЕТОДА ФРОНТАЛЬНОЙ ПОЛИМЕРИЗАЦИИ В ВЫСОКИХ ТЕХНОЛОГИЯХ

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Изначально метод фронтальной полимеризации воспринимался научной общественностью в основном как высокопроизводительный и экологически безопасный метод синтеза полимеров и полимерных композитов. Однако за последние десятилетия выяснилось, что благодаря ее специфике использование метода фронтальной полимеризации приводит к существенным достижениям в области высоких технологий: синтез полимерных нанокомпозитов, синтез высокотемпературных интеркалированных полимерных сверхпроводников, синтез многофункциональных градиентных полимерных материалов и др.

В представленной обзорной статье авторами описываются собственные результаты и международные данные по вышеперечисленным проблемам.

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