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ORIGINAL CONTRIBUTION

I.A. Gritzkova
G.B. Adebayo
I.G. Krasheninnikova
V.A. Kaminsky

The synthesis of polymer suspension with narrow particle size distribution for immunochemical investigations

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I.A. Gritzkova (✉) · G.B. Adebayo
I.G. Krasheninnikova
Moscow State Academy of Fine Chemical Technology
Vernadskiy avenue
86-117571
Moscow
Russia

V.A. Kaminsky
Karpov Institute of Physical Chemistry
Vorontzovo Pole
10-103064
Moscow
Russia

Abstract Heterophase polymerization of styrene in the presence of di-*p*-tolyl-*o*-carbalkoxyphenylcarbinol (DTC) soluble in monomer and insoluble in water, as stabilizer, was investigated. The factors affecting polymer particle diameter, their size distribution and stability were investigated. It was suggested that polymer particles are formed from monomer droplets. The polystyrene suspension with narrow particle size distribution synthesized in the presence of DTC, was used for immunochemical research.

Key words Heterophase polymerization – emulsion – polymer particle – stability – styrene conversion

Introduction

In connection with the problem of getting polymer dispersions with narrow particles size distribution, this article is dedicated to the main methods of their synthesis and factors determining their polydispersity.

Traditional and the most widely known methods of polymer suspension synthesis are emulsion and suspension polymerization.

During the process of emulsion polymerization the size of polymer–monomer particles (PMP) is not directly connected with the sizes of monomer droplets of initial emulsion. According to the theory of Harkins [1, 2], Urzhenko [3, 4], Smith and Ewart [5] the particles are formed upon the entrance of radical into micelles of emulsifier containing monomer.

Recently, it has been proved that PMP are formed not from micelles of emulsifier only, but also from microdroplets of monomer appearing as a result of microemulsification of monomer at the interphase border [4–6].

These different mechanisms of PMP formation lead to a significant width size distribution of PMP in comparison with the predicted theory of micelle mechanism in which PMP are formed micelle of emulsifier only.

In such cases, when PMP are formed mainly from monomer droplets, the particles size distribution of polymer dispersion becomes significantly narrower than the distribution observed when micelles and monomer droplets participated in the formation of PMP.

The processes in which the particles of polymer dispersion are formed directly from monomer droplets of initial emulsion are related to suspension polymerization.

The difference in the size distribution of synthesized polymer particles and the distribution of the initial emulsion droplets results from the coalescence of PMP at the early stage of polymerization.

For the stabilization of monomer droplets and thereafter PMP, water soluble polymeric surface active substances (SAS) are used (such as gelatin, starch, carboxylmethylcellulose, polyvinyl alcohol and so on) which as a rule are characterized with less surface activity than those used in traditional emulsion polymerization, and furthermore, their concentration is approximately ten times lower. This low concentration and less surface activity of polymeric SAS lead to the formation of PMP from monomer droplets less stable and cause their coalescence at the early stage of polymerization and therefore the formation of polymer suspension with wide particle size distribution and sometimes formation of non-spherical polymer particles [7–9].

Although increasing the concentration of SAS leads to higher stability of PMP, the globules of the molecules of polymeric stabilizer appear in water phase, swell with monomer, capture radical from water phase and turn into PMP. PMP formed from the globules of polymeric stabilizer's molecules have the size of 0.2 mkm and the emulsion polymerization proceeds in them with a very high molecular mass. The particle size distribution of polymer dispersion becomes extremely wide.

It is obvious that in the presence of water soluble SAS, the synthesis of stable polymer suspension with narrow particle size distribution by suspension polymerization method has become rather problematic.

The variety of PMP formation mechanisms coupled with coalescence of particles at the early stage of polymerization, make regulating the diameter of polymer dispersion particles and the width of their size distribution rather difficult.

Besides the above-mentioned mechanisms defining the size of particles and their distribution, crushing of monomer droplets also takes place at the beginning of polymerization [10–12].

The peculiarity of this phenomenon of monomer droplets crushing is in its simultaneous occurrence with the increase of viscosity of disperse phase owing to the formation of polymer.

Imagine a situation where the crushing of monomer droplets at the beginning of polymerization becomes the main source of PMP. In that case, it is necessary to exclude the presence of micelles, polymeric globules in the water phase and microemulsification of monomer due to the transfer of SAS at the interphase border. To achieve these conditions, emulsion polymerization of monomers is carried out in the presence of SAS insoluble in water but in a system of oil/water type of emulsion.

Water insoluble SAS of our choice decreases the interphase tension and creates oil/water type monomer emulsion, although not stable and easily exfoliated when stirring is stopped. It differs from traditional SAS, in the presence of which the initial monomers' emulsions are rather stable.

It could be assumed that the formation of polymer at the initial stage of the process increases PMP stability and assists in preventing coagulation [13, 14]. If the crush of monomer droplets is preserved at the initial stage of polymerization and provided the necessary number of PMP and their stability, are adequate, the polymer suspension with narrow particle size distributions could be obtained.

But the question is, under what condition can the interphase adsorption layer of the particles providing their stability be created?

It is obvious that such interphase layer should be characterized by high reological strength and should contain ionogenic groups in its composition capable of forming a double electric layer during their orientation on the interphase border.

Only joint action of electrostatic and structural-mechanical factors of stabilization realized in the interphase adsorption layer can provide the stability of particles against coalescence, particularly, at the initial stage of polymerization.

Electrostatic stabilization of particles is easily obtained due to the presence on the surface of PMP ionogenic groups, fragments of molecule of initiator entering the polymer chains and orientating the interphase border.

Potassium persulphate widely used for emulsion polymerization initiation is a good provider of ionogenic groups. The number of ionogenic groups necessary for the stabilization of dispersed particles is easily regulated by the concentration of the initiator. While the structural–mechanical stabilization of particles is provided by the formation of polymer at the interphase adsorption layer, this explains the stability of PMP and their narrow particle size distribution during emulsion, polymerization in the absence of emulsifier, polymer dispersions which are stable during storage for a period of one month and in weak electrolyte solutions.

The use of SAS with voluminous hydrophobic fragments orienting on the interphase border enhances the stability of polymer dispersions.

Di-*p*-tolyl-*o*-carbalkoxyphenylcarbinol (DTC) meets the requirement of SAS mentioned above. Polystyrene dispersions with narrow particle size distribution, stable in 0.3 M NaCl solution and stable for six month period of storage were synthesized in the presence of DTC.

The aim of this work is to investigate the mechanism of PMP formation in the presence of water insoluble DTC

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and the factors determining the diameter of particles and their size distribution.

Investigations are complicated by the difficulties in analysing the initial monomer emulsion and the initial stage of polymerization.

Experimental

Materials

Styrene (purity 99.6%), stabilized with 1% hydrohynone, was purified from stabilizer by using aqueous NaOH solution, rinsed with water to neutral pH, dried over calcium chloride and distilled twice under reduced pressure (b.p. 36 °C/2.6 × 10^3 Pa).

Initiators

Azoisobutyronitril (AIBN) technical grade was twice overcristallized from methanol, vacuum dried to constant weight, m.p. 101 °C. Benzoil peroxide and layroil peroxide – technical products were twice precipitated with methanol from chloroform solution, vacuum dried till constant weight, m.p. 106–108 °C and 55–56 °C correspondingly.

Purified potassium persulphate, $K_2S_2O_8$, hydroperoxide isopropylbenzene, hydroperoxide isopropylcyclohexylbenzene, rongalyt were used.

Stabilizers

Standard di-*p*-tolyl-*o*-carbalkoxyphenylcarbinol was (in comformity with TU 38.10368-86). Polyvinyl alcohol (PVA) MM = 55 000 were used.

Solvents

Tetrahydrofuran, analytical grade, acetone, diethyl ether, methanol, ethanol, chloroform and toluene were used without further purification.

Dispersion medium

Water – bidistillate.

Results and their discussion

The goal of the investigation of heterophase polymerization of styrene in the presence of stabilizer DTC soluble in monomer is to determine the conditions of synthesis of polymer suspensions with narrow particle size distribution which are stable during polymerization and likewise during storage and in weak solutions of electrolytes.

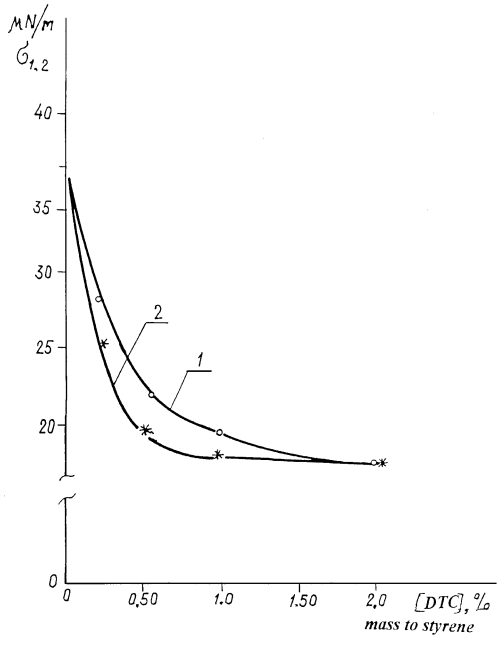
The investigation began with the study of surface-active properties of DTC under 25 and 70 °C (temperature of polymerization).

Figure 1 shows the isotherms of interphase tension. Table 1 shows colloid-chemical properties of DTC. It is clear that DTC is surface-active and its surface-activity grows with temperature increase.

Polymer dispersions were obtained by the polymerization of styrene, initiated with potassium persulphate, with the volume ratio of monomer to water phases used for both the syntheses of suspension for immunochemical research and for the syntheses of polymers and polymer suspensions of general purpose (i.e. 1:9 and 1:2, respectively).

Conversion-time curves, characterizing the process of styrene polymerization under the two chosen monomer–water phases ratio are shown in Fig. 2. It is seen that polymerization proceeds with a period (100 and 180 min correspondingly) during which the formation of particles takes place and afterward, at a constant polymerization rate until 70% conversion of the monomer. The durations of polymerization up to complete monomer conversion is 12 and 28 h, respectively. Figure 2 also shows the conversion-time curves for styrene polymerization in mass initiated with azoisobutyronitril (DAK) both in the presence

Fig. 1 The isotherms of interphase tension at the border of styrene solution of DTC and water at: 25 °C – curve 1; 70 °C – curve 2



and in the absence of DTC (curves 3 and 4, respectively). It is clear that styrene polymerization proceeds at the same rate, that is DTC does not limit the polymerization process. Table 2 and Fig. 3A and B show the analytical data of monomer droplets' sizes in the initial emulsion and the sizes of PMP at 10% less styrene conversion, i.e. at the stage of PMP formation, obtained with the help of laser spectroscopy (malvern zetasizer) and electron microscopy.

Table 1 Colloid-chemical properties of DTC under 20 and 70 °C

$\sigma_{1,2}$ [mH/m]	$\Gamma_{\max} \times 10^6$ [mol/m^2]	G [mHm^2/mol]	T [°C]
18	3.2	18	25
18	5.0	25	70

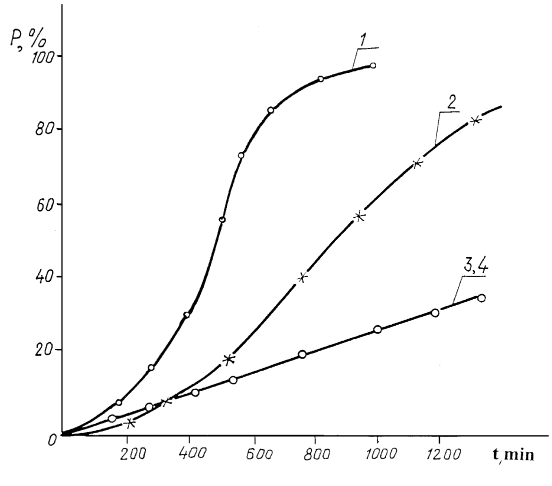


Fig. 2 Conversion-time curves, received under styrene polymerization under concentration $K_2S_2O_8$ and DTC = 1.0% mass to styrene

According to these results the sizes of styrene droplets of the emulsion obtained in the presence of DTC under stirring at 800 turn/min varies in the interval of 4–10 mkm.

With the initiation of polymerization (styrene conversion 1.5–5%) the size of the monomer droplets decreases significantly and at styrene conversion of $\approx 5.5\%$, the average size of styrene droplets is 0.251 mkm, i.e. intensive crushing of droplet takes place.

Crushing of monomer droplets on initiation was confirmed by the data obtained on polymerization of styrene in static condition. The polymerization took place at the temperature 70 °C at the border water solution of potassium persulfate and styrene solution of DTC. The monomer phase was carefully introduced on the water phase and the whole system was left 48 h after which the white viscous layer which had been formed on the border of the phases was removed and analyzed. It was polystyrene dispersion in water, and the styrene conversion in PMP was 90%.

Electro-microscopic analysis showed that polymer suspension contains particles with wide size distribution (Fig. 4A and B). This may be explained by the formation of particles from monomer droplets of different sizes, which seems, to have occurred not only from crushing of monomer droplets due to chemical reaction, but also with their microemulsification as a result of mass transfer (of styrene oligomer formed in the water phase) through the interpase border [15]. Majority of particles (80%) were formed from monomer droplets.

In the process of styrene polymerization, in the presence of DTC, very few or no changes in the size of PMP were observed. Polymer suspensions are characterized

Table 2 The variations in average particle size increase conversion of styrene

Conversion %	Dry reminant, r	Average diameter of particles [mkm] (Laser spectroscopy)	Average diameter of particles [mkm] (Electron microscopy)
0	—	4–10	—
1.5	0.144	1.7	—
5.5	0.513	0.251	0.430
10.5	0.96	0.320	0.440
15	1.4	0.308	0.440
21	1.9	0.276	—
27	2.5	0.344	0.440
32	3.0	0.360	—
40	3.9	0.360	—
60	5.66	0.407	0.450
87	8.18	0.300	0.450
91	8.5	0.405	—

Polymerization conditions: concentration of $K_2S_2O_8$ – 1% wt part to styrene, volume ratio styrene/water – 1:9, concentration of DTC – 1% wt. part to styrene, polymerization temperature – 70 °C.

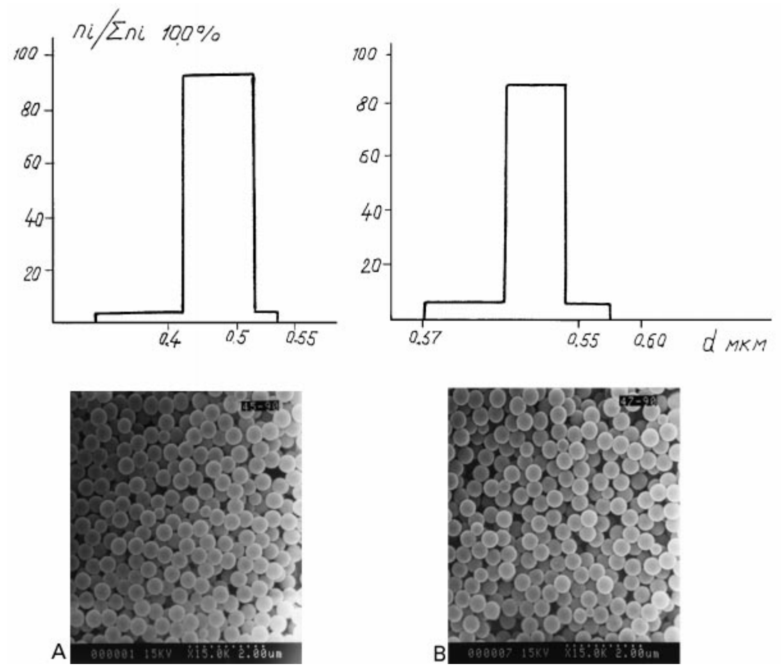


Fig. 3 (A) Electromicrophotography of suspended particles under 10% conversion of styrene and histogram of particle size distribution: phase ratio 1:9, $T = 70\,^{\circ}\mathrm{C}$ $[K_2S_2O_8] = [\mathrm{DTC}] = 1\%$ wt. part to styrene. (B) Electromicrophotography of suspended particles under 99.8% conversion of styrene and histogram of particle size distribution: phase ratio 1:9, $T = 70\,^{\circ}\mathrm{C}$, $[K_2S_2O_8] = [\mathrm{DTC}] = 1\%$ wt. part to styrene

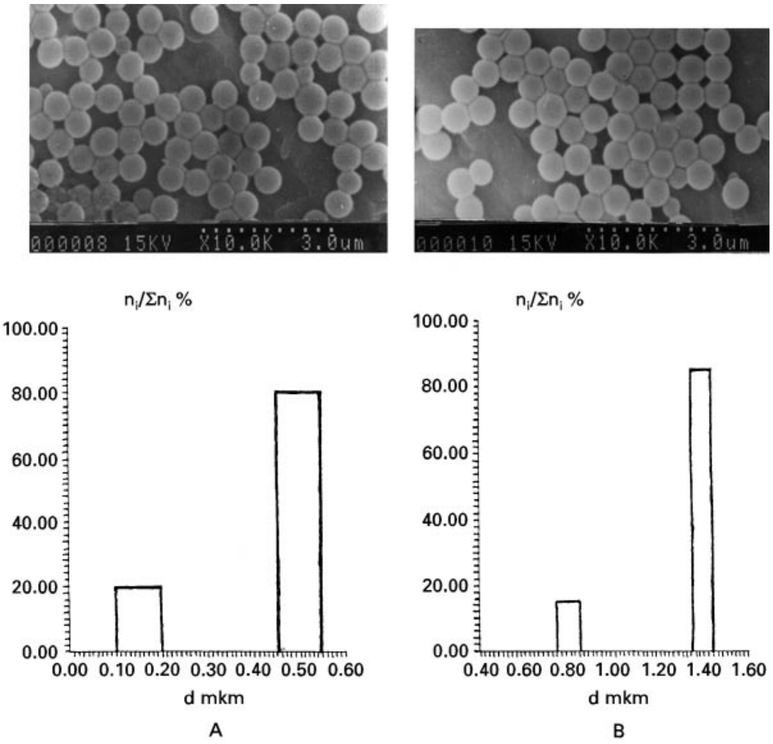


Fig. 4 Electromicrophotography of polystyrene particles suspension synthesized under static condition and histogram of particle size distribution: phase ratio (monomer/water) = 1:9, temperature = $70\,^{\circ}\mathrm{C}$, concentration of DTC = 1% wt. part to styrene, (A) $[K_2S_2O_8] = 1\%$ wt. part to styrene, (B) $[\mathrm{DAK}] = 1\%$ wt. part to styrene

by stability in the process of polymerization which evidently is connected to the formation of structural-mechanical and electrostatic factors of stabilization in the interphase layer.

Additional information on the kinetics and topochemical nature of styrene polymerization in the presence of DTC may be obtained from the data on molecular masses and molecular mass distribution MMD.

Table 3 The change of MM and polymer polydispersity during polymerization of styreme in the presence DTC as stabilizer

N n/n	Conversion of styrene, %	M_w	M_n	M_z	M_η	M_w/M_n
1	5	64	—	—	60	—
2	10	65	—	—	61	—
3	20	66.8	8	329	62	7.83
4	30	99.5	28	347	—	—
5	50	99.9	30	268	64	—
6	75	114	14	117	65	7.9
7	100	355	56	1000	326	6.3
8	In presence of DTC AIBN 100	340	50	800	300	6.8
9	In absence of DTC AIBN 100	350	46	760	310	6.8
10	Static condition of polymerization					
a	$K_2S_2O_8$	418	69	134	269	6.99
b	AIBN	346	54.6	876	179	6.34

[$K_2S_2O_8$] – 1% (wt. part to styrene, [DTC] – 1% wt. part to styrene; polymerization temperature – 70 °C, phase ratio monomer/water = 1:9, 8,9 – mass polymerization of styrene, 70 °C, AIBN – 1% mass to styrene.

Table 3 shows the dependence of molecular masses and MMD of polymers on the degree of monomer conversion. It is obvious that in the process of polymerization of styrene in mass, the molecular masses of polymers are closely related in value to those obtained during polymerization of styrene in the absence of DTC. This indicates that DTC does not participate in chain transfer reaction during polymerization.

With the increase of styrene conversion, growth in molecular masses is observed and under the complete monomer conversion they are five times over those observed at the beginning of polymerization.

The molecular mass changes significantly and polydispersity (M_w/M_n) varies in the interval 6.3–7.0.

The most important factors influencing molecular mass of polymer in the process of polymerization may be pointed out as the growth of viscosity in the particles with increase of monomer conversion and the decrease of thickness of near surface layer by increased concentration of the radicals, firstly by getting into the particles from the water phase.

These factors are essential for the mathematical modeling of polymerization process.

One of the tasks of this work is to determine the factors influencing the diameter of particles. As such the influence of initiator and stabilizer concentrations, phase ratio monomer/water and temperature on the size of polymer dispersion particles were investigated.

It was shown that the dependence of styrene polymerization rate is to the power 0.5 of initiator concentration and this is true for concentration of initiator up to 30% (weight part to styrene). While the molecular masses are inversely proportional to the concentration to the power 0.5.

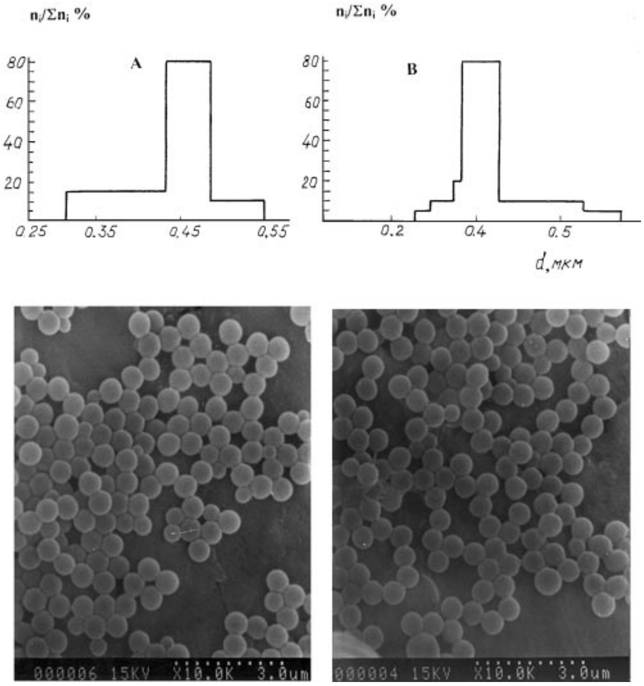


Fig. 5 Histograms of particles sizes distribution and electromicrophoto graphy of particles synthesized at $T_{pol} = 70$ °C, concentration of $K_2S_2O_8$ – 1% wt. part to styrene and DTC (A) 0.5, (B) 1.5% wt. part to styrene

The average size of polymer microspheres depends less on initiator concentration within the limit under this investigation, all polymer suspensions have narrow particles size distribution (Fig. 5A and B).

The dependence of polymerization rate on DTC concentration is observed in the range of concentration from 0.5 to 2.0% (weight part to styrene). Increasing the concentration of DTC up to 4% (wt. part to styrene) does not affect the rate polymerization. This phenomenon differs from the one observed under traditional emulsion poly merization where the rate of polymerization process grows proportionately to increase in emulsifier concentration but similar to those observed during suspension polymerization of styrene, rate which does not depend on the concentration of the stabilizer.

The average size of polystyrene microspheres practically does not depend of DTC concentration and is equal to 0.45 mkm according to the data of electronic microscopy (Fig. 6A and B).

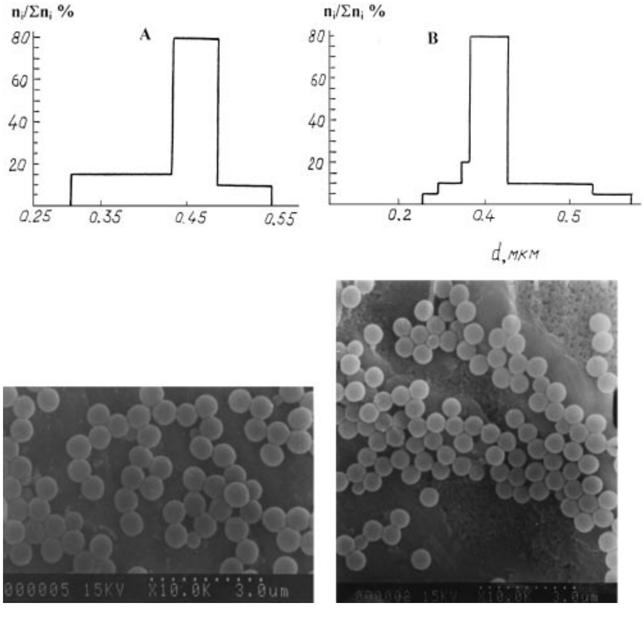
The diameter of polymer suspension particles should depend on the quantity of monomer in the emulsion.

To confirm this influence, styrene polymerization was carried out under constant concentrations of potassium persilfate and DTC equal to 1% weight part per styrene and polymerization temperature 70 °C, the phase ratios (styrene/water) were 1:200; 1:100; 1:50; 1:9; 1:4; 1:2.

Molecular masses change correspondingly, i.e. grow with the increase of monomer concentration up to 10% or more.

The conversion time curves are shown in Fig. 7. It is clear that with increasing concentration of styrene within the interval of phase ratio from 1:200 to 1:50, polymerization rate grows. Further increase of monomer concentration up to 10% and more leads to the decrease rate of polymerization.

Fig. 6 Histograms of particles sizes distribution and electromicrophotography of particles synthesized at $T_{\mathrm{pol}} = 70\,^{\circ}\mathrm{C}$, concentration of $K_2S_2O_8$ – 1% wt. part to styrene and DTC (A) 0.25, (B) 3% wt. part to styrene



The observed dependence may be explained by the growth in the particle size with the increase of volume ratio styrene/water and the process of polymerization by suspension mechanism. The results are shown in Table 4.

Thus changing the volume ratio of monomer/water we can change the mechanism of styrene polymerization from emulsion to suspension one and produce polymer suspensions with narrow particle size distributions and particle diameters in the interval of 0.08–1.20 mkm.

The impact of the nature of initiators on the diameter of particles and their size distribution was investigated.

Styrene polymerization was initiated with potassium persulfate, azoisobutyronitril and hydroperoxideizopropylbensine, under equal molar concentration of 3.36×10^{-2} mol/l and DTC of concentration equalling 1% wt part to styrene, polymerization temperature was 70 °C, phase ratio (styrene/water 1:9. Fig. 8A–C shows the changes in particle size of polymer suspensions (monomer conversion of 99.8%).

These results prove that polymer dispersion with narrow particle sizes distribution may be obtained only in the presence of potassium persulfate.

The influence of polymerization temperature on particle diameters and their size distribution, are shown in Fig. 9A–E. These results are of peculiar interest.

The concentrations of DTC and potassium persulfate were equal to 1% wt. part of styrene and polymerization was carried out at different temperature 50, 70 and 80 °C.

Fig. 7 Conversion-time curves at $T_{\mathrm{pol}} = 70\,^{\circ}\mathrm{C}$, phase ratio (monomer/water) equals to: (1) 1:50, (2) 1:100, (3) 1:200, (4) 1:9, (5) 1:4, (6) 1:2

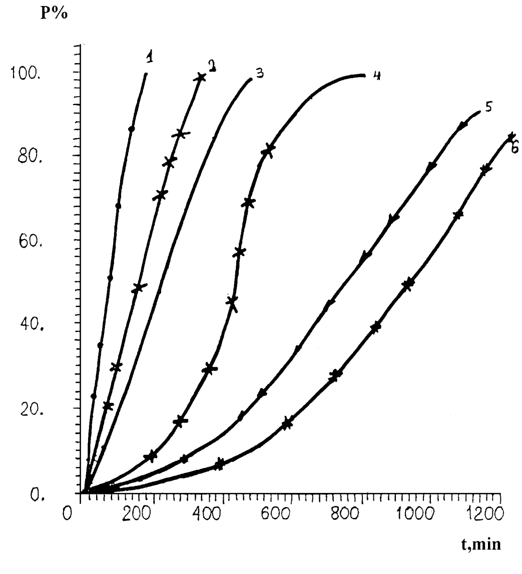
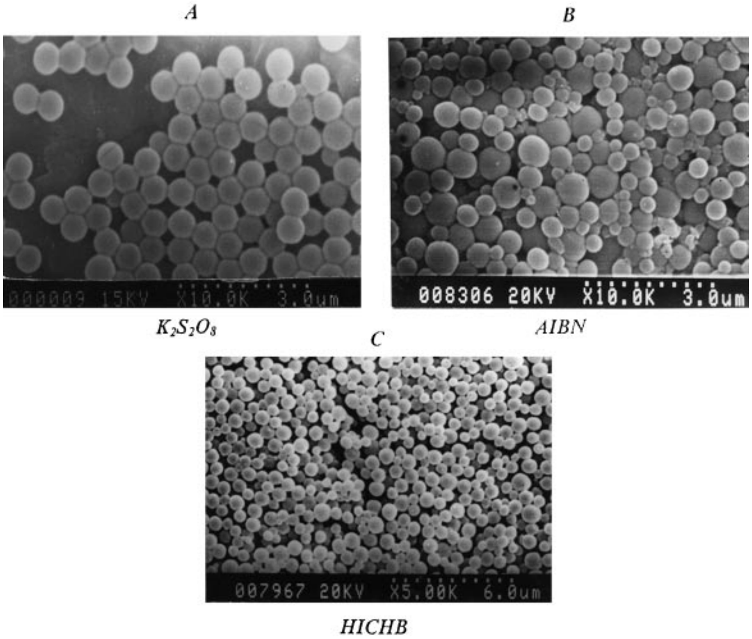


Table 4 The dependence of molecular mass of polymer on concentrations of stabilizer, initiator and phases ratio

$[K_2S_2O_8]$ [%]	[DTC] [%]	Phases ratio	M_w	M_n	$M_z \times 10^{-3}$	M_η	M_w/M_n	D [mkm]	Particles vol. $V \times 10^{-4}$ l of styrene
wt. part of styrene									
0.1	1.0	1:9	634	26	3039	780	24.3		
0.3	1.0	1:9	493	32	1600	412	12.5		
0.5	1.0	1:9	440	40	1530	404	10.9		
1.0	1.0	1:9	355	56	1170	372	6.3		
1.5	1.0	1:9	313	26	1020	313	11.9		
2.0	1.0	1:9	242	40	630	208	5.2		
3.0	1.0	1:9	243	18	1721	472	11.9		
4.0	1.0	1:9	233	17	998	172	13.7		
		1:2	—	—	—	—	—	1.2	
		1:6	—	—	—	—	—	0.6	
1.0	1.0	1:4	235	42	957	1680	5.6	0.8	2700
1.0	1.0	1:9	397	21	2370	325	18.3	0.45	480
1.0	1.0	1:50	220	22	1080	208	9.6	0.15	
1.0	1.0	1:100	190	23	850	179	8.1	0.10	6.23
1.0	1.0	1:200	147	7	939	190	20.8	0.08	
1.0	0.1	1:9	317	21	2240	276	15.0		
1.0	0.5	1:9	531	30	3360	337	17.6		
1.0	2.0	1:9	498	31	2700	316	16.1		
1.0	3.0	1:9	547	31	2730	368	17.7		
1.0	4.0	1:9	429	45	1270	–	7.3		



$K_2S_2O_8$ AIBN HICHB

Fig. 8 (A–C) Electromicrophotography of polystyrene suspension particles obtained under initiation of polymerization by $K_2S_2O_8$, AIBN and HICHB, with equal molar concentration, 3.36×10^{-2} mol/l, concentration of DTC = 1% wt. part to styrene, polymerization temperature = 70 °C and volume ratio styrene/water = 1:9

The conversion time curves are shown in Fig. 9A. It is seen that the periods of PMP formation are 340, 100 and 45 min, respectively, and the total polymerization times, were 40, 12 and 8 h, respectively.

The Polymer suspensions obtained under 50 °C has wide particle size distributions through the whole period of polymerization process. The diameter of particles change in interval of 0.4 to 1.6 mkm (Fig. 9B).

It may be supposed that owing to a long period of PMP formation, as a result of slow polymerization rate, the process of particle coalescence takes place because of low stability of PMP.

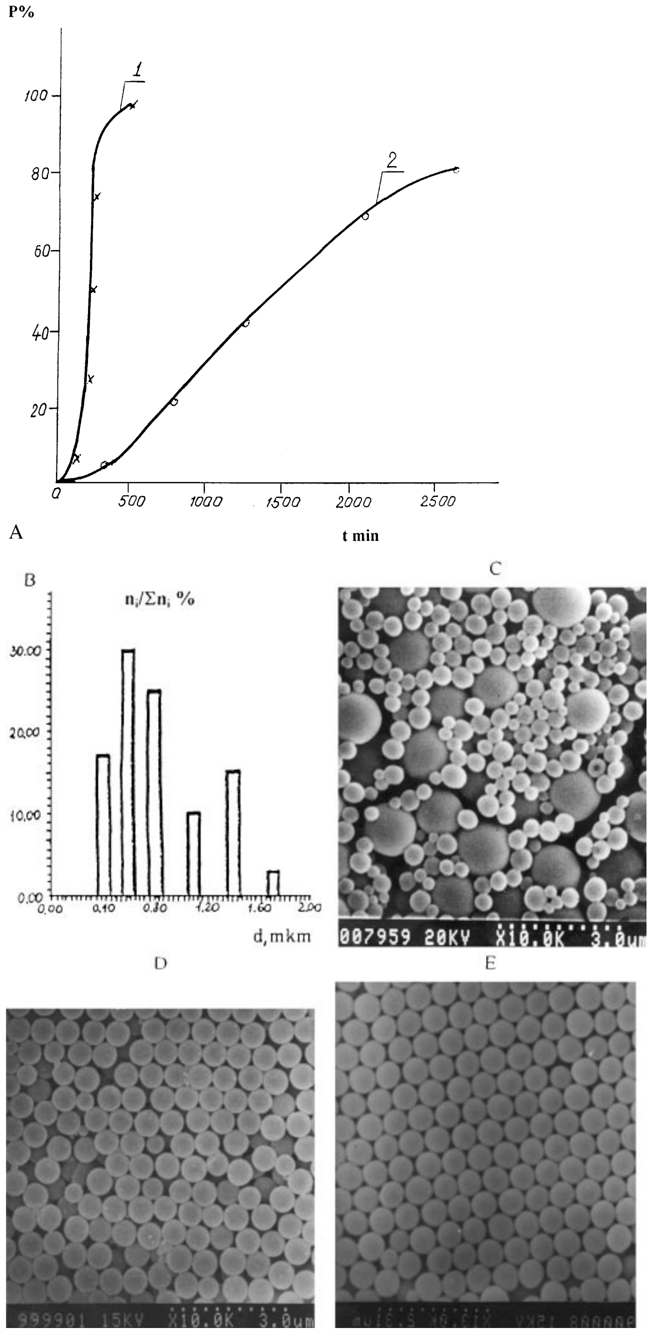


Fig. 9 (A–E) Conversion-time curves, [I] = [DTC] = 1% wt part to styrene, phase ratio (styrene/water) = 1:9, polymerization temperature – curve 1 at 80 °C, curve 2 at 50 °C. Histograms of particles sizes distributions (B) – at $T_{\mathrm{pol}} = 50$ °C) and electromicrophotography of particles synthesized at T_{pol} = C – 50 °C, D – 70 °C, and E – 80 °C. Concentration of $K_2S_2O_8$ – 1% wt. part to styrene and DTC – 1% wt. part to styrene

The rate of polymer formation under 70 °C is much higher than what it is under 50 °C, so that already at 3% of monomer conversion, its contribution in strengthening the interphase layer of PMP is rather significant and particles become stable to coalescence and have narrow size distribution.

The investigation of styrene polymerization in the presence of DTC under two temperature regimes (50 and 80 °C) was carried out. Firstly, initiating the polymerization was performed at 50 °C till 5% conversion of monomer occurred and then the temperature was sharply increased to 80 °C and under this temperature the process was carried on till conversion of monomer was completed. Secondly, the temperature condition were changed, i.e. initiation of the polymerization was carried out at 80 °C till 5% monomer was converted and temperature was sharply decreased to 50 °C and under 50 °C the process was continued till the conversion of monomer was complete. In both cases, polymer suspension particles were narrow but the particles differed in diameter: the particles received under 50 °C had larger diameter.

It follows that under 50 °C, monomer crushing is slower than at 80 °C. Fig. 9 (C–E) show microphotographs of polymer suspension particles, during styrene polymerization under different temperature conditions.

Polymerization proceeded under similar conditions, i.e. equal concentrations of DTC and initiator, PMP formed at 70 °C turned out to be stable to coalescence. The contribution of polymer in the strengthening of interphase adsorption layer becomes very convincing; that is to say that the rate of polymerization is of significant importance. The higher the polymerization rate, the faster the formation of tough interphase adsorption layer and as such the stability of formed PMP commenced at the beginning of polymerization.

Synthesized polymer suspensions were successfully used as albumin carriers in diagnostic test-systems, working on the bases of latex-agglutination reaction.

Conclusions

This investigation shows that during the polymerization of styrene initiated by potassium persulfate in the presence of DTC polystyrene suspension was received with narrow particle size distribution and diameters in the interval of 0.08–1.2 mkm, stable during polymerization process, storage and as well as in weak electrolyte solutions.

It was shown that the mechanism of particle formation is the crushing of monomer droplets during the polymerization initiation.

It was proved that the stability of polymer suspension during synthesis, the size of particles and their size distribution significantly depend on polymerization temperature, concentration of monomer and potassium persulfate (initiator).

It was revealed that synthesized particles of polymer suspensions may be used in immunochemical research as albumin carriers.

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