POLYMERIZATION

Heterophase Polymerization of Styrene in the Presence of Biodegradable Surfactants

V. V. Istratov[a],*, E. V. Milushkova[b], S. M. Levachev[c], S. A. Gusev[d], I. A. Gritskova[b], and V. A. Vasnev[a]

[a] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia
[b] Lomonosov State University of Fine Chemical Technology, pr. Vernadskogo 86, Moscow, 119571 Russia
[c] Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia
[d] Research Institute of Physicochemical Medicine, Federal Medical and Biological Agency,
Malaya Pirogovskaya ul. 1a, Moscow, 119435 Russia
*e-mail: slav@ineos.ac.ru
Received June 1, 2015;
Revised Manuscript Received August 3, 2015

Abstract—Linear and branched copolylactides of various structures are synthesized and characterized. Polystyrene suspensions with various particle diameters are obtained via heterophase polymerization with the use of copolylactides as biodegradable surfactants. The influence of the surfactant structure on the polymer microsphere size and the type of size distribution is studied.

INTRODUCTION

Heterophase polymerization is a highly efficient method of synthesis making it possible under certain conditions to obtain polymers with a narrow diameter distribution. The production conditions of PS and PMMA dispersions with poorly soluble surfactants (such as diparatolylcarbalkoxyphenylcarbinol, oligoglycolmaleinatebanzoates, monoalkylphthalates, and organosilicon surfactants) as stabilizers were determined in [1–5]. Note that poor solubility in water is a key requirement imposed on the surfactants used in heterophase polymerization. In this case, polymer–monomer particles (PMPs) are formed via a single mechanism, namely, from microdrops of the monomer, and have a narrow size distribution. The characteristics of the obtained polymer particles depend on the chemical structures of the used surfactants [6].

A substantial disadvantage of the industrial production of emulsion polymers and latexes is the high consumption of emulsifiers; therefore, the problem of the wastewater purification has become highly important and urgent. The prospects for application of biodegradable surfactants lie in the fact that they decompose in the environment into biologically neutral oligomers and low-molecular compounds, a circumstance that substantially simplifies wastewater purification [7, 8]. Amphiphilic copolymers with high biocompatibility obtained on the basis of aliphatic copolyesters whose hydrophilic blocks are formed by polyethers and whose hydrophobic blocks are f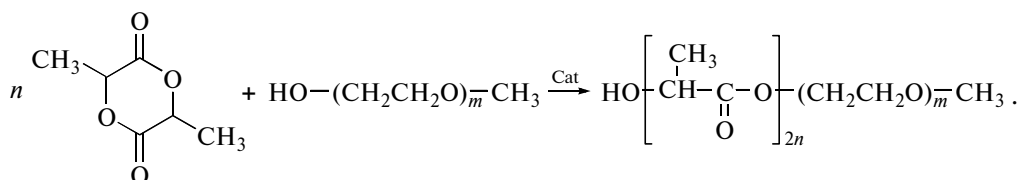ormed by polymers of hydroxyacids (glycolic, lactic, hydroxybutyric, etc.) can be ranged among such biodegradable surfactants. It is known that the hydrolysis of such amphiphilic macromolecules leads to decomposition into environmentally harmless natural hydroxyacids and biocompatible oligomers [9].

It was important to evaluate the application efficiency of the amphiphilic hydroxyacid copolymers as surfactants during heterophase polymerization of styrene. For this purpose, a series of new linear and branched copolylactides containing hydrophobic blocks with a molecular mass exceeding that of the hydrophilic blocks were synthesized. In the present study, the results of the heterophase polymerization of styrene with their participation are discussed.

EXPERIMENTAL

L-Lactide (99%, Aldrich); polyglycerol with $M_w = 500$ and 2000 (synthesized at Johannes Gutenberg University, Mainz, Germany); monomethylene esters of poly(ethylene glycol) with $M_w = 350$, 550, and 750 (MPEG, Aldrich); and tin 2-ethylhexanoate $(Sn(Oct)_2, 95\%, Sigma)$ were used without further purification. Chloroform, methanol, methylenechloride (high-purity, Khimmed) were purified via standard techniques [10].

The linear block-copolymers were obtained through the interaction of *L*-lactide and the monomethylester of poly(ethylene glycol).

$$n \; \text{(L-lactide)} + \text{HO}-(\text{CH}_2\text{CH}_2\text{O})_{\overline{m}}\text{CH}_3 \xrightarrow{\text{Cat}} \text{HO}\left[\text{CH}(\text{CH}_3)-\overset{\text{O}}{\underset{}{\text{C}}}-\text{O}\right]_{2n}(\text{CH}_2\text{CH}_2\text{O})_{\overline{m}}\text{CH}_3.$$

Branched copolymers were obtained via the interaction of *L*-lactide and polyglycerol.

$$n \; \text{(L-lactide)} + \text{polyglycerol} \xrightarrow{\text{Cat}} \text{branched copolymer}$$
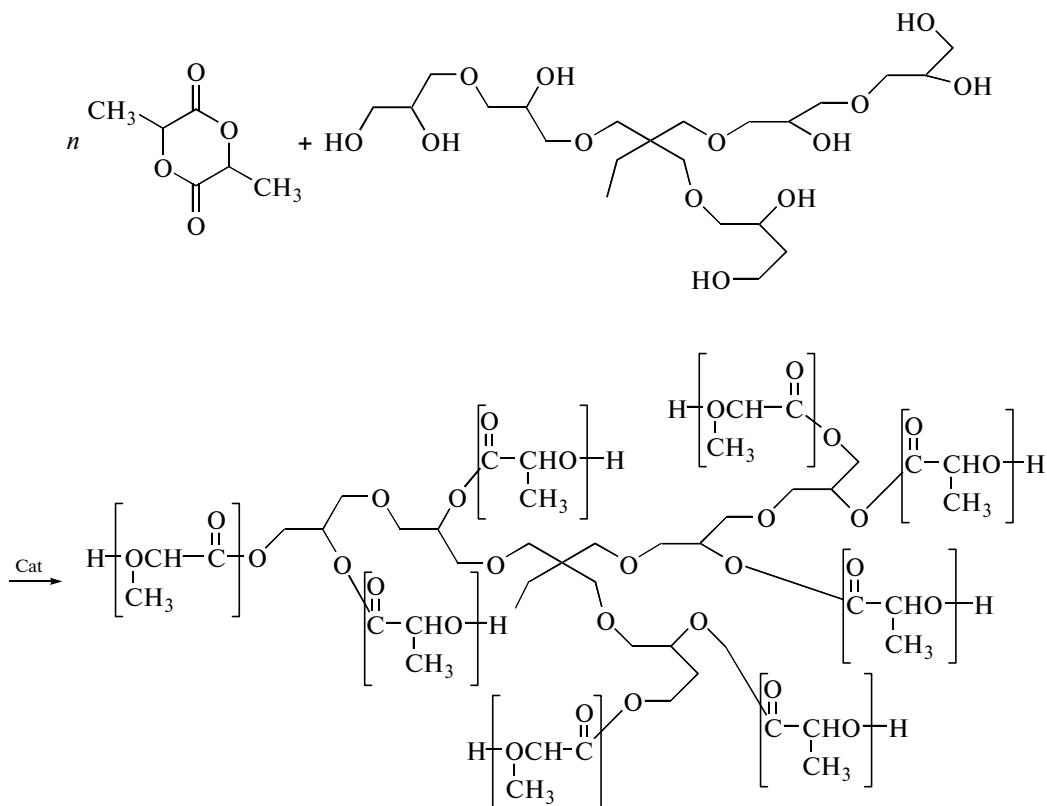
The copolylactides were synthesized via the following technique. A round-bottomed flask equipped with a magnetic stirrer was loaded with 0.1 mol *L*-lactide; 0.00505 mol catalyst, $\text{Sn}(\text{Oct})_2$; and 0.001 mol PEG or polyglycerol. The synthesis was performed in melt at 125°C for 10 h; then, the melt was cooled to room temperature and the polymer was dissolved in chloroform and deposited in methanol. The deposited polymer was filtered and dried in vacuum at 60°C for 48 h.

The IR spectra were registered for the copolymer solutions in CHCl_3 on a Specord M 80 IR spectrophotometer.

The NMR spectra were obtained for 10% solutions of copolymers in CDCl_3 on a Bruker spectrometer with operating frequencies of 600.22 MHz for ^{1}H NMR and 150.94 MHz for ^{13}C NMR (the internal standard was tetramethylsilane) at the Laboratory of Nuclear Magnetic Resonance, Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

Elemental analysis was performed via a gravimetric method by the Group of Special Organic Analysis at the Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

The molecular-mass characteristics of the copolymers were analyzed via GPC on a Waters 150 chromatograph equipped with a PL-GEL 5μ MIX C column (300 mm × 7.5 mm) in THF at a flow rate of 1 mL/min at the Petrov Plastics Institute.

The styrene was polymerized under conditions usually used during synthesis of polymer suspensions for immunochemical investigations [1, 2]. The volume ratio of styrene to water was 1 : 9, the surfactant (copolymers 1–6) and initiator concentrations were 1 wt % per monomer, and the temperature was $80 \pm 0.5°$C. The styrene polymerization rate was studied via a dilatometric method. The emulsion was formed via rotation of the mixing stirrer in a wide part
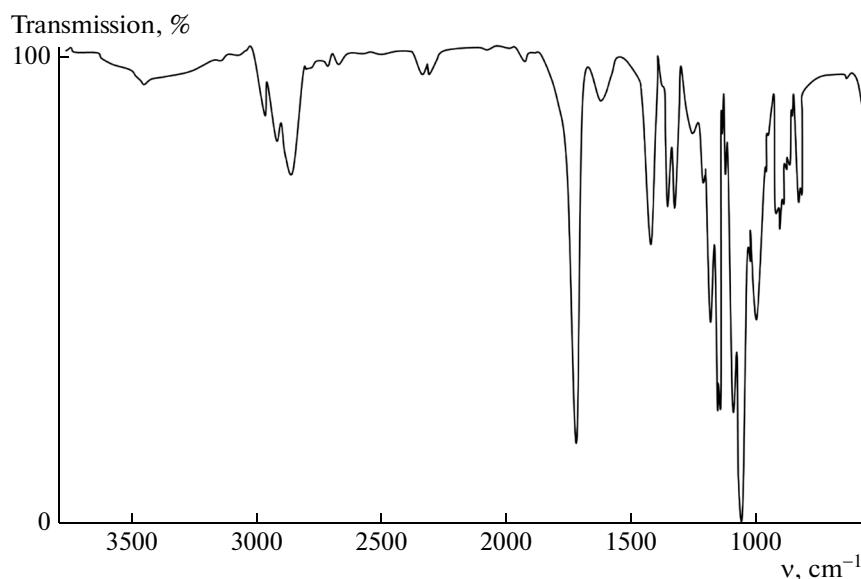
Fig. 1. Typical IR absorption spectra of a (co)polylactide.

of the dilatometer at a rate of 600 rpm. Monomer conversion P was calculated through the equation

$$P = (\Delta h / \Delta h_{max}) \times 100\%$$

Here, Δh is the running change in the level in the dilatometer capillary (cm) and Δh_{max} is the change in the level in the dilatometer capillary corresponding to 100% conversion:

$$h_{max} = V_m \times (\rho_p - \rho_m)/(S \times \rho_p),$$

where V_m is the monomer volume (cm^3), ρ_m and ρ_p are the respective densities of the monomer and the polymer (g/cm^3), and S is the capillary cross-sectional area (cm^2) [1, 2].

The polymer-suspension particle size was determined via the scanning electron microscopy on a Hitachi S-570 apparatus.

The weight-average and number-average diameters of particles, D_w and D_n, were determined from the relationships

$$D_n = \Sigma D_i N_i / \Sigma N_i$$

$$D_n = \Sigma D_i^2 N_i / \Sigma D_i N_i$$

RESULTS AND DISCUSSION

The copolylactides were obtained as dry powders with a symmetric or anisotropic particle form that are easily soluble in acetone and chloroform. The IR spectra of the synthesized copolymers show absorption bands at 3000–2800 cm^{-1}, corresponding to the valence vibrations of the C–H bond of both blocks; in the region of 1768 cm^{-1}, corresponding to the valence vibrations of the carbonyl groups of the ester bond; in the region of 1385–1300 cm^{-1}, corresponding to the

valence vibrations of $-CH_3$ and $-CH_2-$ groups; in the region of 1130–1060 cm^{-1}, corresponding to the ether bond. The presence of the absorption bands at 3700–3670 cm^{-1} confirms the presence of hydroxyl groups in copolymers (Fig. 1).

There are proton signals of $-CH$ and $-CH_3$ groups of the polylactide units at 5.04 and 1.45 ppm, respectively, in the ^{1}H NMR spectra of the synthesized copolymers. In addition, there is a signal corresponding to the protons of $-CH_2-O-$ and $-O-CH_3-$ groups of MPEG (3.50–3.58 ppm and 3.32 ppm) in the spectra of the linear copolymers (Fig. 2, spectra 2–4). The spectra of the branched copolymers have proton signals of $-CH_2-\underline{CH_3}$ (0.88 ppm) and $-\underline{CH_2}-CH_3$ (1.37 ppm) groups characteristic for polyglycerol as well as a wide multiplet signal at 3.00–4.20 ppm, related to protons of $-CH_2-O-$ and $-CH-$ groups of polyglycerol (Fig. 2, spectra 5–8).

The compositions of the synthesized copolymers were determined from the data of NMR spectroscopy and elemental analysis according to the techniques given in [11]. As is seen from Table 1, all compounds were obtained with high yields, and the close values of the theoretical and experimentally determined molecular masses and elemental compositions testify the correspondence of their structures to the assumed structures.

All dependences of styrene conversion on time, independently of the chemical nature of the copolylactides, are S-shaped, a circumstance that is characteristic for heterophase polymerization (Fig. 3). There is an induction period corresponding to the time of PMP formation (~15 min) on the kinetic curves; then,
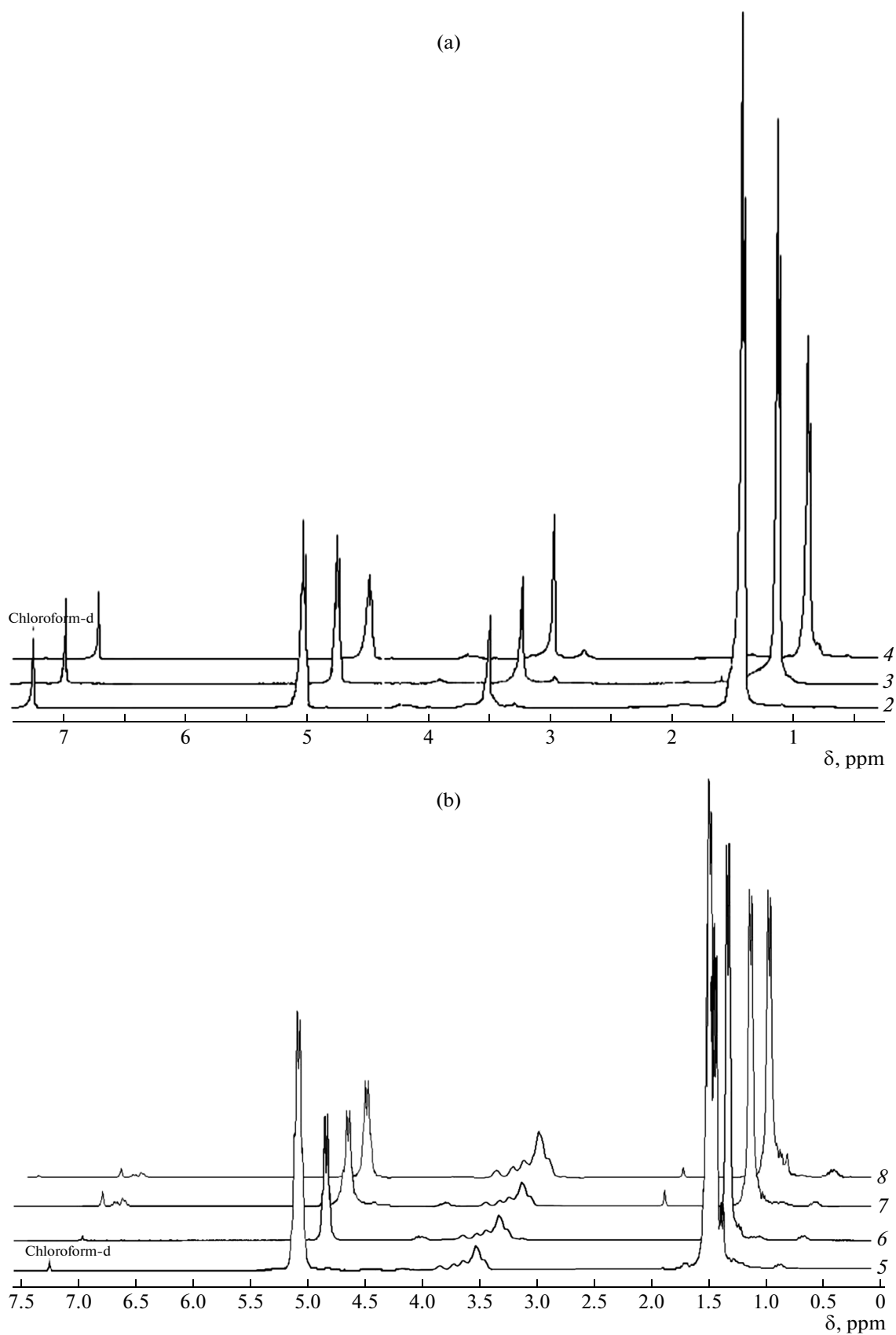
(a)

Chloroform-d

4

3

2

7   6   5   4   3   2   1

δ, ppm

(b)

Chloroform-d

8

7

6

5

7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0   0.5   0

δ, ppm

Fig. 2. ^{1}H NMR spectra of (*2–4*) linear and (*5–8*) branched copolylactides with various contents of polylactide units.
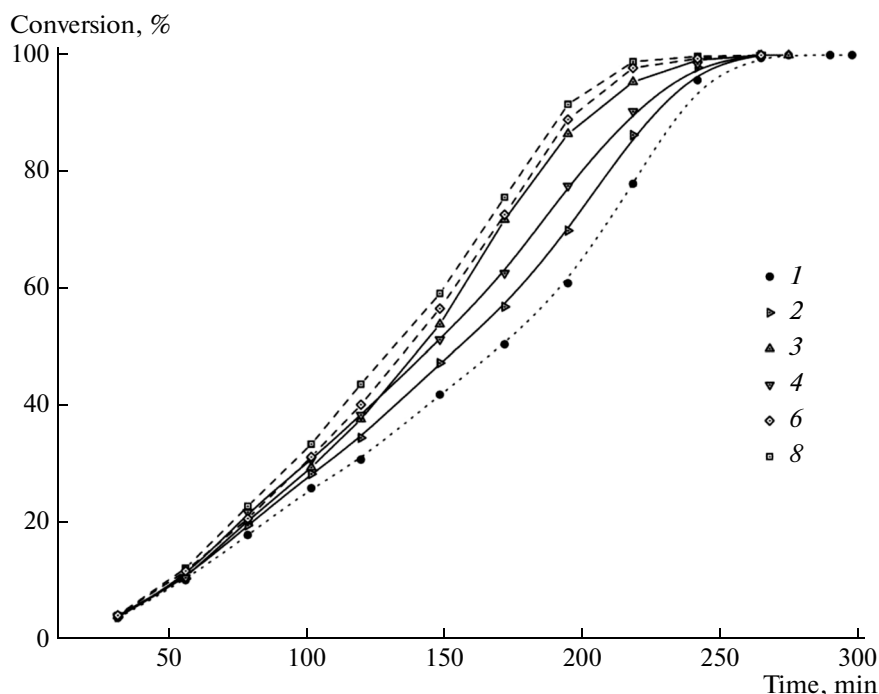
Fig. 3. Dependence of conversion on time during styrene polymerization in the presence of (co)polylactides. Here and therein-after the numbering of curves corresponds to the numbering of the samples in Table 1.

the polymerization proceeds at a high constant rate $((4.4 \times 10^{-7})-(5.5 \times 10^{-7})$ mol/(L s), Table 2) up to complete conversion of the monomer. The time to complete the conversion is 220–270 min.

The polystyrene suspensions synthesized in the presence of polylactide surfactants differ by high stability during polymerization, a circumstance that is indicated by the absence of coagulum. The polystyrene suspension particles are spherical and have a nar-

row size distribution in samples 3 and 5–8 (Fig. 4, Table 2).

The results can be explained in terms of two approaches to the determination of the role of the poorly soluble surfactant used for PMP stabilization.

The first approach [1–5] is based on the formation of the interfacial layer on the particle surface of the surfactant incompatible with the obtained polymer. With an increase in the polymer concentration in the

Table 1. Synthesis conditions and characteristics of copolymers

Copolymer	Monomer		Mole ratio of monomers 1 : 2	Yield, %	$M_n \times 10^{-3}$			M_w/M_n	Elemental composition, %	
	1	2			theory	NMR	GPC		calculated*	found
1	L-Lactide	–	100 : 0	80	20.0	18.1	17.8	1.7	C: 42.9, H: 5.6	C: 46.2, H: 5.4
2	L-Lactide	MPEG-350	99 : 1	80	14.6	10.9	11.6	1.6	C: 50.1, H: 5.8	C: 48.8, H: 5.6
3	L-Lactide	MPEG-550	99 : 1	76	14.8	9.1	10.1	1.6	C: 50.5, H: 6.1	C: 49.0, H: 6.0
4	L-Lactide	MPEG-750	99 : 1	76	15.0	9.3	9.5	1.4	C: 50.4, H: 6.0	C: 48.7, H: 5.6
5	L-Lactide	PG-500	199 : 1	76	29.2	23.5	25.4	2.1	C: 50.0, H: 5.6	C: 48.8, H: 5.4
6	L-Lactide	PG-500	99 : 1	76	14.8	9.4	9.8	1.0	C: 49.9, H: 5.8	C: 49.5, H: 5.7
7	L-Lactide	PG-500	49 : 1	76	7.6	8.4	8.0	2.2	C: 49.9, H: 6.1	C: 45.9, H: 5.7
8	L-Lactide	PG-2000	99 : 1	76	16.3	9.5	10.0	1.4	C: 50.0, H: 5.8	C: 49.1, H: 5.6

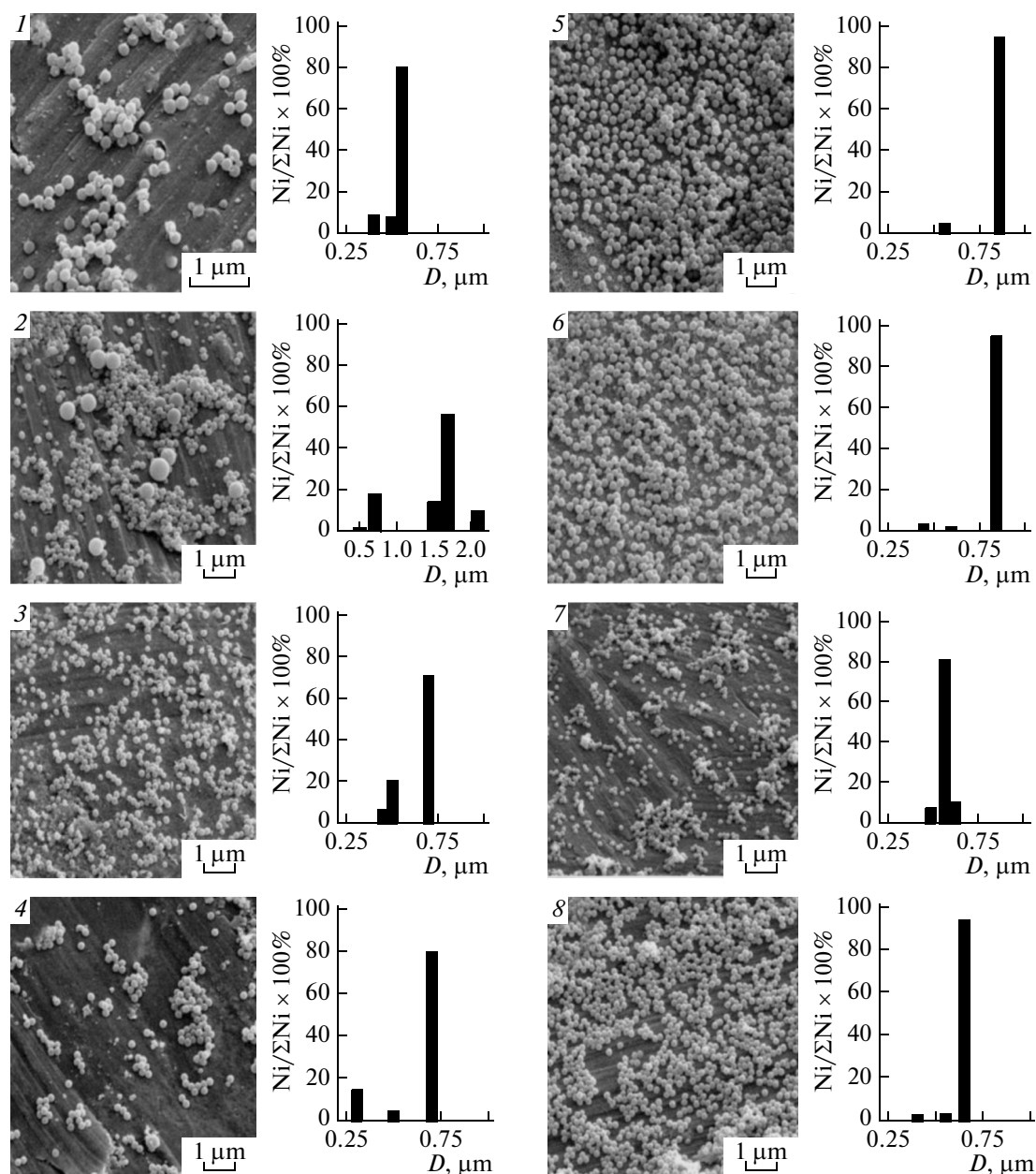* Calculated on the basis of monomer loading.

Fig. 4. Micrographs of polystyrene suspension particles and their size-distribution histograms obtained during styrene polymerization in the presence of (co)polylactides.

PMPs, the surfactant is displaced from the volume to the interface. This results in the formation of particles with the core–shell structure, a circumstance that promotes the aggregative stability of the obtained dispersion. The immobilization of the poorly soluble surfactant at the interface makes it possible to lyophilize the surfaces of PMPs owing to the orientation toward the aqueous phase of the hydrophilic fragments of the surfactant molecules and creates the conditions for the Rehbinder structural–mechanical barrier.

The second approach is based on the geometrical construction of the surfactant molecules at the interface promoting the minimum gradient of polarity during the transition from the aqueous phase to the hydrocarbon. In this case, the results may be explained in terms of the concept of the critical parameters of packing. For example, the idealized diblock–copolymer molecule can be represented as two contacting spheres formed by corresponding blocks; in this case, the sizes of these spheres are proportional to the molecular masses of the copolymer blocks. This macromolecule can be characterized with the use of such parameters as volume v, length l, and block cross-sectional area S_0 (Fig. 5a). The critical parameter of pack-

(a) (b) (c)

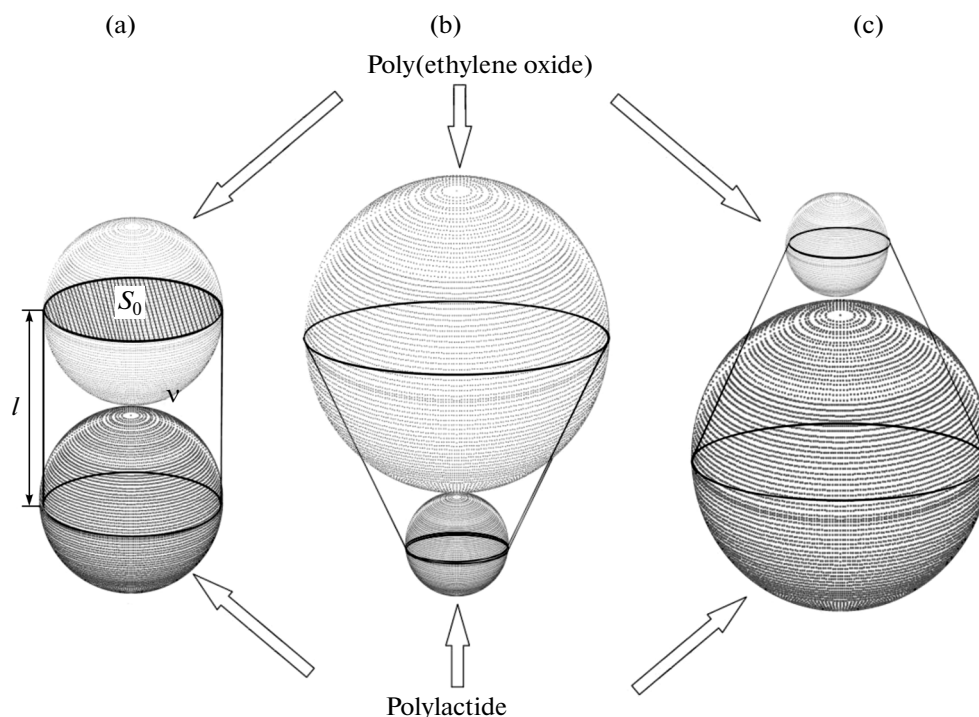Poly(ethylene oxide)

S_0

l

v

Polylactide

Fig. 5. Schematic representation of diblock-copolylactides and main parameters describing their sizes according to theory of critical parameters of macromolecule packing.

ing is determined as the ratio of macromolecule volume v to the product of length l and hydrophilic-block cross-sectional area S_0.

For the macromolecules with similar sizes of the hydrophilic and hydrophobic blocks, such as those given in Fig. 5a, the critical parameter of packing is ≈1. It is known [12, 13] that the aggregation in water of the macromolecules with a critical parameter of packing close to 1 leads to the formation of the lamellar phase. If the size of the hydrophilic block of the macromolecules exceeds the size of the hydrophobic block (Fig. 5b), the critical parameter of packing is less than 1, and an oil-in-water emulsion forms and stabilizes. If the hydrophilic block of the macromolecule is smaller than the hydrophobic block (Fig. 5c), the critical parameter of packing is more than 1 and a water-in-oil emulsion forms and stabilizes. However, in the latter case, dynamically stable oil-in-water emulsions, whose stability is provided by the mixing of the system, is possible.

Exactly copolylactides 2–4 can be among such macromolecules with a critical parameter of packing above 1. It was considered [12] that the change in the block ratio of such polymers affects the interface-surface curvature in water-in-oil emulsions. At the same time, the change in the block ratio in copolymers 2–4 may insignificantly affect the interface-surface cur-

vature in oil-in-water emulsions and, respectively, the PMP sizes during heterophase polymerization.

Such dynamically stable emulsions can be dispersed via two mechanisms. First, this is possible owing to the shear-stress gradient created by the mixing rate and the construction of the stirrer arms. In this case, drops of a large size of about 1–2 μm are formed. Second, the additional dispersion of the emulsion microdrops is possible because of the formation of a microemuslion layer on their surfaces.

Table 2. Characteristics of polymer suspensions obtained with the use of (co)polylactides 1–8 as surfactants

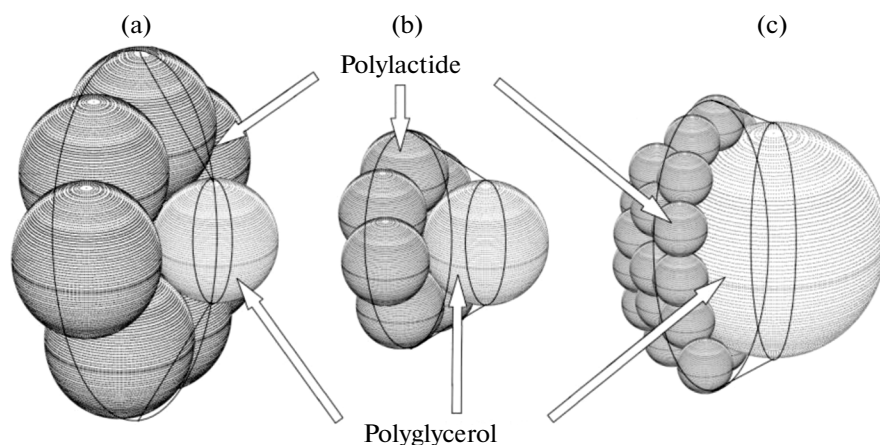| Polymer	$V_p \times 10^7$, mol/L s	d, μm	D_w/D_n	$M_\eta \times 10^{-3}$
1	3.5	0.53	1.03	530
2	4.4	1.09	1.50	595
3	4.5	0.64	1.04	310
4	4.7	0.62	1.11	125
5	4.8	0.82	1.02	295
6	5.1	0.80	1.05	410
7	4.8	0.55	1.01	490
8	5.5	0.63	1.02	260

Fig. 6. Schematic representation of branched copolylactides: (a) polymer 5, (b) polymer 7, (c) polymer 8.

The microemulsification on the monomer microdrop surface is observed as a result of the mass transfer of the components through the interface. Then, a finely dispersed emulsion of the monomer is formed. The presence of the monomer microdrops of various sizes in the initial emulsion is a cause of the formation of polymer suspensions with a bimodal size distribution (Fig. 4).

It is characteristic that, for the branched copolylactides, the suspension-particle size depends on the molecular mass of the hydrophilic block, which, in this case, is polyglycerol: The increase in its fraction leads to a decrease in the suspension-particle size. In this case, the mass ratio of the hydrophobic and hydrophilic blocks is comparable with the values obtained for linear copolylactides (Table 1).

The structure of the branched copolylactides can be presented as several spherical hydrophobic blocks connected by the same sphere of the hydrophobic block (Fig. 6). Comparatively slight changes in the hydrophobic-block volumes (in particular, of polymers 6 and 7) cause substantial changes in surface curvature. As a result, even a comparatively slight change in the molecular mass of the hydrophobic blocks leads to a noticeable decrease in suspension-particle size, a result that is explained by the monomer dispersion via one mechanism.

Polymers 7 and 8 have close molecular masses of the hydrophobic blocks, but the molecular masses of the hydrophilic blocks differ. Nevertheless, the particle sizes of the polystyrene suspension obtained in the presence of these polymers are close (Table 2). With an increase in the molecular mass of the polyglycerol block from 500 to 2000, its functionality rises noticeably (from 8 hydroxyl groups to 28). In the amphiphilic block-copolymers, these hydroxyl groups are replaced with short polylactide blocks. For example, the molecular mass of the hydrophilic block of copolylactide 8 increases 4 times in comparison to that of polymer 7, and the

amount of hydrophobic blocks increases 3.5 times. As a result of such multidirectional effects, the particle size of the polystyrene latex of polymer 8 is slightly higher than that of polymer 7.

CONCLUSIONS

The conditions of the heterophase polymerization determined in the presence of the amphiphilic copolymers of oxyacids with poly(ethylene glycol) or polyglycerol have made it possible to obtain polystyrene microspheres with an average diameter from 0.55 to 0.8 μm that have a narrow size distribution. The investigated surfactants differ by high biodegradability, a phenomenon that is necessary for the development of green-chemistry principles in the field of synthesis of polymer dispersions of different uses.

ACKNOWLEDGMENTS

REFERENCES

1. I. G. Krasheninnikova, Extended Abstract of Candidate's Dissertation in Chemistry (RKhTU, Moscow, 2007).

2. I. A. Gritskova, V. S. Papkov, I. G. Krasheninnikova, and A. M. Evtushenko, Polym. Sci., Ser. A **49** (3), 235 (2007).

3. O. V. Chirikova, Extended Abstract of Candidate's Dissertation in Chemistry (MITKhT, Moscow, 1994).

4. D. I. Shragin, I. A. Gritskova, V. V. Kopylov, E. V. Milushkova, L. A. Zlydneva, and S. M. Levachev, Silicon **7**, 217 (2015).

5. L. A. Zlydneva, Extended Abstract of Candidate's Dissertation in Chemistry (MITKhT, Moscow, 2013).

6. C. Chorng-Shyan, *Principles and Applications of Emulsion Polymerization* (Wiley, New York, 2008).

7. A. M. Fernandez, U. Held, A. Willing, and W. H. Breuer, Prog. Org. Coat. **53** (4), 246 (2005).

8. M. J. Scott and M. N. Jones, Biochim. Biophys. Acta **1508**, 235 (2000).

9. V. A. Vasnev, Polym. Sci., Ser. B **39** (11−12), 474 (1997).

10. W. L. E. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals* (Buttleworth-Heinemann, Oxford, 1998).

11. V. V. Istratov, V. T. Tarasyuk, V. A. Vasnev, and N. A. Borisova, Polym. Sci., Ser. B **55** (3−4), 218 (2013).

12. K. Holmberg, B. Jönsson, B. Kronberg, and B. Lindman, *Surfactants and Polymers in Aqueous Solution* (Wiley, New York, 2002).

13. S. K. Mehta and Kaur. Gurpreet, "Microemulsions: Thermodynamic and Dynamic Properties," in *Thermodynamics*, Ed. by M. Tadashi (InTech, 2011).

Translated by K. Aleksanyan