

Dispersion polymerization of methyl methacrylate in heptane

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The particle size of poly(methyl methacrylate) dispersion is a function of relative molecular mass and concentration of the three-block isoprene—styrene—*isoprene* copolymer operating as a dispersant of the polymer dispersion.

The influence of temperature of polymerization on the particle size of poly(methyl methacrylate) dispersion in the interval 50—90 °C is negligible. In contrast to the results hitherto published, the study of the influence of dispersant on the rate of dispersion polymerization has shown that this rate is influenced by concentration and molecular mass of the polymer dispersant. The polymer dispersant has no capability to influence directly the rate of polymerization. It only regulates the size of arising particles and thus the change in polymerization rate due to dispersant is to be regarded as a result of the influence of the change in size of polymer particles. The rate of dispersion polymerization increases with concentration of the polymer dispersant, *i.e.* with diminution of particles. A similar but more conspicuous dependence appears if polymer dispersants with different molecular mass are used.

Величина частиц полиметилметакрилатной дисперсии является функцией относительной молекулярной массы и концентрации трехблочного сополимера *изопрен—стирол—изопрен*, действующего в качестве дисперсора полимерной дисперсии.

Влиянием температуры полимеризации на величину частиц полиметилметакрилатной дисперсии в интервале 50—90 °C можно пренебречь. В противоположность до сих пор опубликованным результатам, изучение влияния дисперсора на скорость дисперсионной полимеризации показывает, что эта скорость определяется концентрацией и молекулярной массой полимерного дисперсора. Нет никаких оснований, чтобы полимерный дисперсор прямо влиял на скорость полимеризации, он лишь регулирует величину возникающих полимерных частиц, а поэтому изменение скоростей полимеризации в зависимости от дисперсора следует понимать как следствие влияния изменений величины полимерных частиц. Скорость дисперсионной полимеризации возрастает с увеличением концентрации полимерного дисперсора, т.е., с уменьшением величины частиц.

Подобная, но более выраженная зависимость была установлена при использовании полимерных дисперсоров с различной молекулярной массой.

The radical dispersion polymerization of vinyl monomers in nonaqueous media is relatively a new technique of heterogeneous polymerization [1]. Though this technique differs at first sight from the considerably well explored and more than half a century successfully used emulsion polymerization only by dispersion medium, it has been hitherto much less investigated. Although the theoretical models of radical dispersion polymerization have been known since the end of sixtieth years, they have not yet been experimentally sufficiently verified. It is due to complexity of the process of radical dispersion polymerization as well as to energetic crisis of the seventieth years. As aliphatic hydrocarbons are mainly used as dispersion medium for radical dispersion polymerization, the enormous rise in price of crude oil and oil products has brought a loss of the interest of producers of synthetic polymers in this technique. This fact has also affected the publication activity in the region of radical dispersion polymerization. It is a pity because the radical dispersion polymerization has already come into use for the preparation of special polymers and moreover, it represents a highly interesting scientific problem.

The properties of nonaqueous polymer dispersions are dependent on the kind of the used monomer, dispersion medium, dispersant, and method of realization of radical dispersion polymerization. The dispersant — surface-active substance — ensuring the stability of polymer dispersion with respect to precipitation is an important factor affecting the parameters of polymer dispersions. Macromolecular compounds are mainly used for stabilization of polymer dispersions in nonaqueous media because the common low-molecular surface-active substances used for stabilization of aqueous polymer emulsions lose their efficiency in nonaqueous media. The block and grafted copolymers belong among efficient dispersants of nonaqueous polymer dispersions provided one of their components (block, grafted branch) is insoluble and the second component is soluble in the chosen dispersion medium. The insoluble components of copolymers are adsorbed on polymer particles of polymer dispersion, while the soluble blocks solvated by dispersion medium form a layer about the particles which prevents the aggregation of these particles. This type of stabilization of polymer dispersions is called steric stabilization [2]. The grafted copolymers are mainly used in practice as dispersants for dispersion polymerization because of relative simplicity of their preparation. However, they are not suitable for exact quantitative study of dispersion polymerization because they are for the most part polydisperse in relation to chemical composition as well as molecular mass. Some investigations, in which well-defined two-block polystyrene—dimethylsiloxane copolymers were used for dispersion polymerization of methyl methacrylate, were described recently [3].

The aim of this study is to contribute to the knowledge of the kinetics and mechanism of radical dispersion polymerization of methyl methacrylate in heptane. The influence of relative molecular mass and concentration of polymer dispersants on the course of polymerization and properties of the arisen poly(methyl methacrylate) dispersions was investigated. The three-block copolymers of styrene with isoprene of the isoprene—styrene—styrene type (ISI) and some commercial three-block copolymers Craton G of Shell with inverse sequence of the components, *i.e.* styrene—styrene—styrene were used as polymer dispersants. As for the commercial copolymers Craton G, the sequence of the structural isoprene units was hydrogenated (SHIS).

Experimental

The solvents (heptane, toluene, cyclohexane, and isobutyl alcohol) were anal. grade chemicals (Lachema, Brno). Dibenzoyl peroxide (Koch and Light) was purified by precipitation from chloroform solution by means of methanol.

Methyl methacrylate (Chemical Works, Žilina) was deprived of stabilizer by successive shaking with aqueous solutions containing 10 mass % of NaOH, 10 mass % of sulfuric acid, and 10 mass % of Na₂CO₃ and subsequent washing with distilled water to neutral reaction. Methyl methacrylate thus purified was dried over CaCl₂ and stored in a refrigerator at -15 °C. Immediately before use, it was distilled under reduced nitrogen pressure (100 Pa). Nitrogen used in electric bulb industry was purified by flowing through a column heated to 200 °C and packed with active charcoal containing reduced copper and subsequently it was dried over silica gel.

The three-block copolymers of styrene with isoprene were prepared by anionic polymerization according to the procedure described in paper [4]. The relative molecular mass as well as the composition of the used three-block copolymers is given in Table 1.

Table 1

Characteristics of three-block copolymers [4]

Copolymer	(M_r) _N (PS) ^a	(M_r) _N (PI(PHI)) ^a	(M_r) _N	ASB ^b
ISI-1	6100	2 × 7400	21000	0.41
ISI-2	13700	2 × 16600	47000	0.41
ISI-3	34200	2 × 41400	117000	0.41
ISI-4	51400	2 × 62300	176000	0.41
SHIS-1 ^c	2 × 7155	38700	53000	0.37
SHIS-2 ^d	2 × 11150	60300	83000	0.37

a) Relative number average molecular mass of polystyrene (M_r)_N (PS), polyisoprene (M_r)_N (PI), and hydrogenated polyisoprene (M_r)_N (PHI) blocks (segments).

b) Ratio of molecular masses of anchoring and soluble block. (Anchoring — Soluble — Balance) [5].

c) Craton^R G 1650.

d) Craton^R G 1652.

The poly(methyl methacrylate) dispersions were prepared by thermostating the reaction mixture in sealed glass ampoules for 4 h in nitrogen atmosphere at $(50 \pm 0.2)^\circ\text{C}$. The reaction mixtures were obtained by dissolving the required quantity of the polymer dispersant (0—0.3 g) in *n*-heptane (7.5 cm^3) and mixing this solution with the solution of dibenzoyl peroxide (0.045 g) in methyl methacrylate (3 cm^3). After expiration of the determined reaction time, the ampoule was opened and the polymer dispersion was diluted with 10 cm^3 of *n*-heptane. A portion of the dispersion thus diluted was centrifuged ($f = (5\text{—}8) \times 10^3 \text{ min}^{-1}$). The concentration of the dispersant nonadsorbed on polymer dispersion occurring in the solution over the precipitate formed by centrifugation was determined gravimetrically (drying) and the concentration of the nonconsumed methyl methacrylate was ascertained by gas chromatography (gas chromatograph Perkin—Elmer F 11, column packed with Carbowax 1500 (10 mass %) on Chromaton NAW DMSC (0.1—0.250 mm), internal standard: isobutyl alcohol).

In a similar way, we also prepared reaction mixtures for the DSC measurements (microcalorimeter DSM-2M, USSR). The weighed amounts were approximately 10.8 mg. The filling of aluminium dishes with the reaction mixture as well as the hermetic closure of these dishes took place in a dry box in atmosphere of purified nitrogen. The rate of liberation of reaction heat was observed under isothermal conditions (70°C) as a function of reaction time. Before measurement, the instrument was calibrated by means of the known temperatures and heats of fusion of indium and very pure chemicals (Fischer Thermometric Standards). The value of the latent heat of fusion of indium (28.47 J g^{-1}) was taken from paper [6].

The turbidimetric method described in paper [7] was used for evaluating the particle size of polymer dispersions. In principle, it is similar to earlier methods [8, 9]. The parameters of distribution function were calculated with a computer Siemens 4004 by using the iterative method and the trapezoidal rule of numerical integration [7]. The turbidities of poly(methyl methacrylate) dispersions were measured with a spectrophotometer Specord UV VIS (Zeiss, Jena) at the wavelengths of the used radiation, *i.e.* 300 nm and 600 nm. If need be, the dispersions were diluted with heptane.

The turbidimetric determination of the size of particles of poly(methyl methacrylate) dispersions was verified by measuring the particle size with an electron microscope (Jeol, type JSM 35).

For determining the limiting viscosity number of poly(methyl methacrylate), the diluting type of the Ubbelohde viscosimeter was used. From the limiting viscosity number $[\eta]$ obtained in toluene at 25°C , the relative molecular mass of poly(methyl methacrylate) was calculated according to the following equation [10]

$$\{[\eta]\} = 7.1 \times 10^{-5} (M_r)_v^{0.73} \quad (1)$$

In order to obtain poly(methyl methacrylate) without polymer dispersant, the poly(methyl methacrylate) dispersions were extracted with cyclohexane at the boiling point. The precipitated poly(methyl methacrylate) was centrifuged and extracted again with cyclohexane at the temperature of boiling. This procedure was three-times repeated. This procedure brought about that practically all polymer dispersant passed into solution and poly(methyl methacrylate) was obtained as a product insoluble in cyclohexane.

Results and discussion

Influence of the relative molecular mass and concentration of dispersant on the particle size of polymer dispersion

The following empirical formula was derived [11] for nonaqueous polymer dispersions

$$\bar{d} = K\rho^{-a} \quad (2)$$

This relationship expresses the dependence of the diameter \bar{d} of particles of polymer dispersion on the concentration ρ of dispersant. The value of constant K for a given dispersion medium depends on the character of the used dispersant. The value of constant a varies in the range 0.2—1 according to the hitherto published data [11]. Fig. 1 represents relationship (2) in logarithmic form for some of the

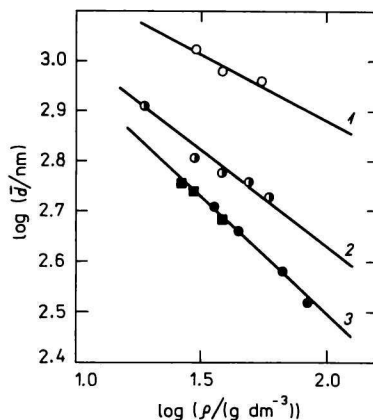


Fig. 1. Variation of diameter \bar{d} (nm) of the particles of poly(methyl methacrylate) dispersions with concentration ρ (g dm⁻³) of polymer dispersant. Concentration of polymer dispersant is referred to methyl methacrylate.

1. ISI-2; 2. ISI-3; 3. ISI-4 (●), ISI-4 with stirred polymerization mixture (■).

investigated polymer dispersions. The necessary data are taken from Table 2. The relative molecular mass of polymer dispersant has considerable influence on the size of particles and the value of the constant a (+0.36 for dispersant ISI-2, +0.40 for dispersant ISI-3, and +0.46 for dispersant ISI-4) slightly increases with relative molecular mass of polymer dispersant. The highest stabilizing efficiency (manifesting itself by formation of small particles of polymer dispersion and high portion of the dispersant adsorbed on polymer particles) is exhibited by the polymer dispersant with highest relative molecular mass (ISI-4). The size of particles of polymer dispersion increases and simultaneously the portion of the adsorbed dispersant decreases with decreasing relative molecular mass of polymer dispersant at its equal concentration. The low value of stabilizing efficiency of dispersants with relatively low molecular mass causes formation of the aggregates of particles, as

Table 2

Average particle size of poly(methyl methacrylate) dispersions in heptane

Dispersant	ϱ^1	ϱ^2	\bar{d}^3	\bar{d}^4
	g dm^{-3}	g dm^{-3}	nm	nm
ISI-1	80	<4	1600 ⁵	2800 ⁵
	60	<4	1800 ⁵	3000 ⁵
ISI-2	100	52.0	830	820
	80	37.6	870	—
	60	30.6	970	950
ISI-3	20	18.3	—	1200
	100	60.7	480	465
	80	50.0	515	—
	60	39.0	525	530
	40	30.4	575	—
	20	18.7	730	—
	10	10.0	—	850
ISI-4	100	83.0	300	—
	80	66.2	345	—
	60	45.0	415	400
	40	36.1	460	—
ISI-4 ⁶	100	38.7	431	420
	80	30.2	490	—
	60	26.7	505	500

1. Concentration of dispersant referred to monomer.

2. Concentration of dispersant adsorbed on the surface of particles of polymer dispersion, *i.e.* the portion utilized for dispersion stabilization (referred to monomer).

3. Average size of particle diameter of polymer dispersion determined turbidimetrically.

4. Average size of particle diameter of polymer dispersion determined by electron microscopy.

5. Inconsistency of the values of particle diameter of polymer dispersions obtained by turbidimetry and electron microscopy is a consequence of aggregate formation in the system. The applicability of turbidimetric determination of particle size is limited, besides other things, for particles of spherical shape [8, 9]. The aggregates do not satisfy this condition.

6. In this case, the polymerization mixture was stirred by turning the ampoules slowly round the cross axis ($f = 60 \text{ min}^{-1}$) in thermostating bath.

observed in the case of dispersion containing dispersant ISI-1 (Fig. 2). The aggregates are formed by association of a greater number of smaller particles. It is interesting that the primary particles constituting the aggregate as well as the aggregates themselves are almost monodisperse.

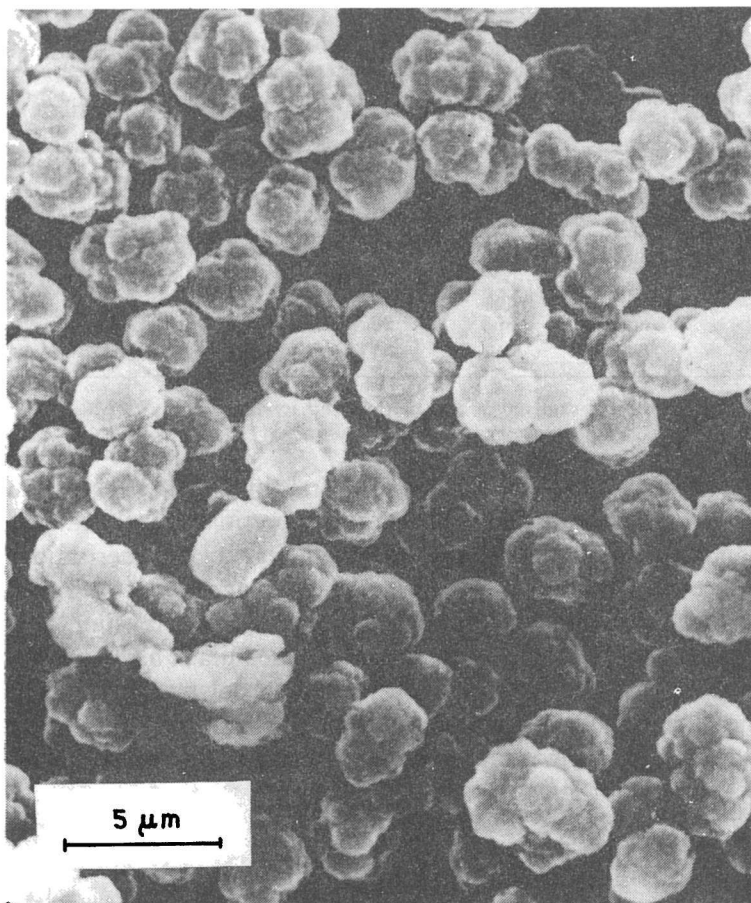


Fig. 2. Poly(methyl methacrylate) dispersion of 80 g dm^{-3} concentration (referred to methyl methacrylate) prepared with dispersant ISI-1. Electron microscope.

Influence of the relative molecular mass and concentration of dispersant on the rate of dispersion polymerization

In contrast to the data published in literature [11], it has been found that the concentration as well as the molecular mass of dispersant influences the rate of dispersion polymerization (Table 3). The data about the conversion of methyl methacrylate reveal the dependence on concentration as well as relative molecular mass of dispersant. In order to elucidate the influence of relative molecular mass and concentration of dispersant on the rate of dispersion polymerization, we

Table 3

Conversion of methyl methacrylate in dispersion polymerization in the presence of polymer dispersants of varying concentration ρ . Dispersion medium: n-heptane; polymerization time 4 h; temperature 50 °C

$\frac{\rho}{\text{g dm}^{-3}}$	100	80	60	40	20	10
ISI-1	—	58.8	59.4	—	—	—
ISI-2	83.0	81.8	80.4	77.5	73.6	—
ISI-3	86.2	86.8	80.3	83.4	78.5	74.7
ISI-4	89.8	89.4	84.9	82.2	78.0	—

a) Concentration of dispersant referred to methyl methacrylate.

performed microcalorimetric measurements and investigated the dependence of the liberated polymerization heat on time for dispersion polymerization. The rate of liberation of polymerization heat reflecting the rate of polymerization increases from the outset of polymerization, which is in good agreement with the theory of dispersion polymerization. This theory implies the growth reaction of dispersion polymerization only in polymer particles, *i.e.* in a medium of high viscosity and thus the gel effect appears already in very early stages of polymerization. In Fig. 3, the rates of liberation of polymerization heat as a function of monomer conversion are shown for dispersion polymerization in the systems with different concentrations of

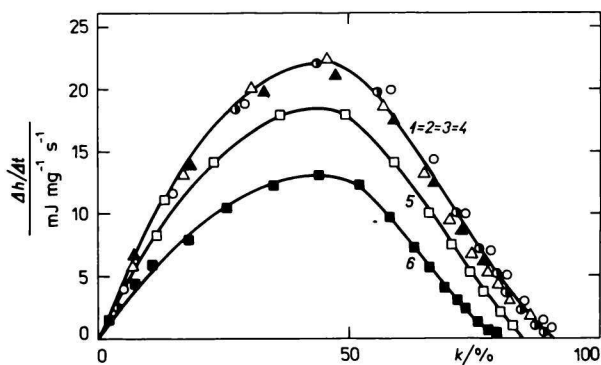


Fig. 3. The rate of liberation of reaction heat $\Delta h/\Delta t$ for dispersion polymerization of methyl methacrylate in n-heptane as a function of methyl methacrylate conversion. Data normalized for unit amount of methyl methacrylate in reaction mixture. Temperature 70 °C. The calculation of monomer conversion is given in the text. Concentration of dispersant ISI-3 ($\rho/(\text{g dm}^{-3})$) is referred to methyl methacrylate.

1. 100 (○); 2. 80 (●); 3. 60 (△); 4. 40 (▲); 5. 20 (□); 6. without dispersant (■).

dispersant ISI-3. The values of monomer conversion for a given time interval of dispersion polymerization were obtained by integrating the relationship $\Delta h/\Delta t = f(t)$ and comparing the obtained value of the liberated reaction heat of dispersion polymerization of poly(methyl methacrylate) Δh (for a certain weighed amount of polymerization mixture) with the value $\Delta h = 55.5 \text{ kJ mol}^{-1}$ of the reaction heat of methyl methacrylate polymerization [12]. Fig. 4 represents the analogous relationships for dispersion polymerizations in the systems containing dispersants with different relative molecular mass in equal concentration.

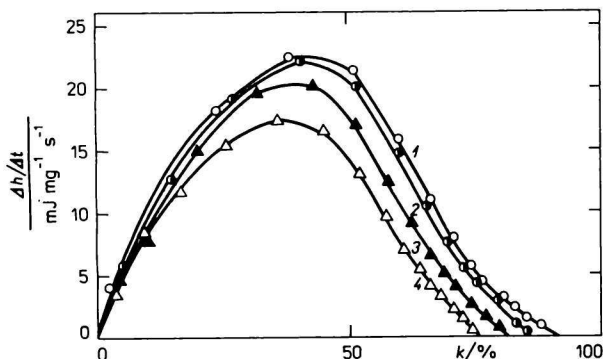


Fig. 4. The rate of liberation of reaction heat $\Delta h/\Delta t$ for dispersion polymerization of methyl methacrylate in *n*-heptane as a function of methyl methacrylate conversion. Data normalized for unit amount of methyl methacrylate in reaction mixture. Temperature 70 °C. The calculation of monomer conversion is given in the text. Concentration of dispersants: 100 g dm^{-3} (referred to methyl methacrylate).

1. ISI-4; 2. ISI-3; 3. ISI-2; 4. ISI-1.

A comparison of the curves describing the liberation of reaction heat as a function of monomer conversion (Fig. 3) shows the relation between the concentration of dispersant (particle size) and the rate of polymerization. While curves 1–4 are closely akin, curve 5 enables us to observe a decrease in reaction rate and curve 6 demonstrates a clear change in polymerization kinetics. Similar results are also presented in the paper by Barrett and Thomas [11]. However, these authors interpret them so that the almost identical curves of polymerizations with higher content of dispersant are to be regarded as an evidence of nonexistence of the influence of particle size on polymerization rate and the character of the curves corresponding to polymerizations with lower content of dispersant which exhibit deviations is justified without further explanation by aggregate formation. Nevertheless, it is not clear why we should make principal distinction between the primary particles and aggregates though we must admit that these aggregates could

arise in the investigated system. From the view-point of the problem concerning the influence on kinetics, we may, as a matter of fact, consider the aggregates to be fully equivalent particles which differ from the primary particles merely by their size or shape (surface area). It results from this reasoning that a connection between particle size and polymerization rate exists and appears only for greater difference between the sizes of particles or manifests itself for smaller difference between the sizes of particles so feebly that a change in reaction rate cannot be revealed by the DSC method.

The fact that the change in polymerization rate cannot be attributed to some particular effect of aggregates is evidenced by Fig. 4 which represents the curves expressing the liberation of polymerization heat in the systems with greater differences in particle sizes while only curve 4 evidently corresponds to aggregates. As for other curves, the formation of aggregates may be very likely ruled out.

The differences between the curves in this figure are evident, even between the curves corresponding to such systems where no formation of aggregates is to be expected.

It follows that the influence of particle size of dispersion on polymerization rate may be considered to be proved. It is possible to interpret or at least explain the cause of this influence on the basis of the following mechanism:

We may assume by right that the mobility of growing oligomers inside particles is considerably limited. The poorly mobile oligomer radicals are adsorbed by the particles and do not diffuse inside them, but accumulate on their surface. The smaller is the total area of the surface of particles, the greater is the possibility of termination of the oligomer radicals by recombination, which results in decrease in the rate of dispersion polymerization provided larger particles arise in the course of polymerization (their overall surface decreases).

Influence of the relative molecular mass and concentration of dispersant on the relative molecular mass of arising polymer

The relative molecular mass of poly(methyl methacrylate) prepared by dispersion polymerization (Table 4) is considerably high, which is in harmony with the assumption of a reduced termination of macroradicals (gel effect) in dispersion polymerization. This table makes possible to see a clear but not very conspicuous dependence of relative molecular mass of the arising polymer on concentration of the used dispersant as well. In general, we may deduce that the relative molecular mass of the arising polymer decreases with decreasing concentration and relative molecular mass of the dispersant, i.e. with increasing size of the particles of dispersions (Table 2). As the relative molecular mass of polymer is in direct relation to the rate of polymerization (its growth reaction), we may consider these

Table 4

Relative viscosity molecular mass of poly(methyl methacrylate) prepared by dispersion polymerization in n-heptane

a) Dependence on concentration of polymer dispersant ISI-3

ρ /(g dm ⁻³) of dispersant (referred to monomer)	100	80	60	40	20	10
$(M_r)_v \cdot 10^{-5}$	6.08	4.95	5.42	5.02	4.82	4.56

b) Dependence on the kind of dispersant; concentration of polymer dispersant 80 g dm⁻³, referred to monomer

Dispersant	ISI-1	ISI-2	ISI-3	ISI-4
$(M_r)_v \cdot 10^{-5}$	3.19	3.50	4.95	10.8

results to be further evidence for the influence of the particle size of polymer dispersion on the rate of dispersion polymerization.

Influence of temperature on the particle size of polymer dispersion

The results are summarized in Table 5. The measured sizes of particles of polymer dispersion vary in the range 425—460 nm. Thus the temperature has

Table 5

Variation of particle size of polymer dispersions with temperature of dispersion polymerization
Polymer dispersant ISI-3; $\rho = 100$ g dm⁻³ (referred to monomer)
Polymerization time: 4 h

θ /°C	50	55	65	70	75	80	85	90
\bar{d} /nm	465	450	455	450	455	450	425	430

negligible influence on the final size of particles of polymer dispersion in the investigated temperature interval.

Influence of the order of sequences in three-block copolymer of styrene with isoprene on dispersion polymerization of methyl methacrylate

The presented results concerning the use of three-block copolymers of styrene with isoprene of the type ISI confirmed the suitability to applying these copolymers as stabilizers of the poly(methyl methacrylate) dispersion. However, the suitability of applying a three-block copolymer of styrene with isoprene having an inverse order of particular sequences, *i.e.* a copolymer of the type SIS remained problematic. The commercial three-block copolymer of styrene with hydrogenated structural isoprene unit was used as model for this type of copolymer. The copolymer Craton G exhibits approximately equal solubility in heptane and equal proportion of both components as copolymers of the type ISI (Table 1).

However, the use of the copolymers Craton G has shown that these copolymers are not at all efficient for stabilizing a poly(methyl methacrylate) dispersion in heptane. The expansion of the central block of copolymer soluble in heptane evidently hinders the adsorption of the terminal segments of three-block copolymer sticking in the surface of polymer particles and favours the intermolecular interaction between insoluble blocks of copolymer, which brings about complete disappearance of the stabilizing ability of this kind of three-block copolymer.

References

1. Barrett, K. E. J., in *Dispersion Polymerization in Organic Media* (Barrett, K. E. J., Editor), Chap. 1. Wiley, London, 1975.
2. Osmond, D. W. J. and Waite, F. A., in *Dispersion Polymerization in Organic Media* (Barrett, K. E. J., Editor), Chap. 2. Wiley, London, 1975.
3. Dawkins, J. V. and Taylor, G., *Polymer* 20, 599 (1979).
4. Šušoliak, O., *CSc. Thesis*. Polymer Institute, Centre for Chemical Research, Slovak Academy of Sciences, Bratislava, 1983.
5. Walbridge, D. J., in *Dispersion Polymerization in Organic Media* (Barrett, K. E. J., Editor), Chap. 3. Wiley, London, 1975.
6. *Selected Values of Standards*, Circular 500, 660 (1961).
7. Zollars, R. L., *J. Colloid Interface Sci.* 74, 163 (1979).
8. Mie, G., *Ann. Phys.* 25, 377 (1908).
9. Van de Hulst, H. C., *Light Scattering by Small Particles*. Wiley, New York, 1957.
10. *Polymer Handbook* (Brandrup, J. and Immergut, B., Editors), Second Edition, Chap. IV. Wiley—Interscience, New York, 1975.
11. Barrett, K. E. J. and Thomas, H. R., in *Dispersion Polymerization in Organic Media* (Barrett, K. E. J., Editor), Chap. 4. Wiley, London, 1975.
12. *Polymer Handbook* (Brandrup, J. and Immergut, B., Editors), Second Edition, Chap. II. Wiley—Interscience, New York, 1975.

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