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Effect of Polydispersity on the Morphological Symmetry of Poly(methyl methacrylate)-block-polystyrene Copolymer Films

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Abstract

The effect of polydispersity of the poly(methyl methacrylate) block on the morphological symmetry of the films of diblock copolymers synthesized by two-stage reversible addition-fragmentation chain transfer polymerization of methyl methacrylate and styrene was investigated. Increasing polydispersity from 1.11 to 1.53 of PMMA includes a transition from lamellar symmetry with a periodicity of 67 nm to cubic symmetry of spherical domains (58 nm), via a mixed lamellar-spherical symmetry.

Keywords: polydispersity, diblock copolymers, morphology, reversible addition-fragmentation chain transfer polymerization

1 Introduction

One of the key physicochemical properties of block copolymers is their ability to undergo microphase separation, which, from a thermodynamic perspective, is interpreted as an “order–disorder transition” [1–10]. This process yields highly ordered supramolecular nanostructures such as spherical and cylindrical micelles, alternating and perforated lamellae, and bicontinuous structures [6–8]. The microphase behavior of monodisperse AB diblock copolymers (DC) (with polydispersity index, $PDI \equiv M_w/M_n < 1.1$) is well understood both theoretically and experimentally. It is governed by the block lengths (N_A and N_B), their volume fractions ($f_A = N_A/N$, $f_B = N_B/N$, where $N = N_A + N_B$ is the total number of segments in the copolymer chain), and the Flory–Huggins interaction parameter χ , which quantifies the incompatibility between the A and B blocks [9,10].

Recently, due to the development of reversible deactivation radical polymerization (RDRP) techniques has enabled the synthesis of copolymers with diverse macromolecular architectures, including block copolymers from a wide range of functional monomers. However, the PDI of polymers synthesized by RDRP is often higher than 1.1, especially on an industrial scale. At PDI exceeding 1.1, the broad chain length distribution perturbs the packing of macromolecules within microphase-separated domains. Consequently, the PDI, along with the copolymer composition, the block lengths, and the Flory–Huggins parameter χ , constitutes a key parameter that governs the

equilibrium morphology of diblock copolymers and their resultant properties [11–17]. As a result, nanostructure formation from polydisperse block copolymers has become a topic of considerable interest.

Various methods have been developed to control the molecular weight distribution (MWD) of copolymers. In particular, polydisperse block copolymers can be achieved either by mixing narrowly dispersed block copolymers/homopolymers with different compositions and molecular weights [11,15–20] or by creating the desired total MWD directly during the polymer synthesis process [11,12,14,21–24].

Polymer blending is a commonly used and simple method for controlling the width and shape of the MWD, but it has some drawbacks. In particular, it requires the synthesis of multiple precursor narrowly dispersed polymers under stringent conditions and can lead to multimodal MWDs [11,14,18,19]. Furthermore, achieving a specific target MWD (including higher moments such as skewness) requires precise calculation of blend ratios, for instance via the moments of mathematical distributions [20].

Recent efforts to overcome the limitations of the blending approach have focused on achieving a desired MWD directly during polymer synthesis. These strategies involve the selection of chain transfer agents (CTAs) with tailored reactivity in RDRP [11,12,14,21–23] or the use of appropriate catalysts in anionic polymerization [24–26]. Among the more recent strategies of reversible addition-fragmentation chain transfer (RAFT) polymerization, which is a type of RDRP, one approach involves mixing two CTAs with different activities, allowing for tuning of dispersity between the extremes achieved by each individual CTA, while maintaining a monomodal molecular weight distribution [27]; the concept of mixed CTAs has also been applied to photoinduced electron/energy transfer RAFT polymerization.[28] Another method employs pH-switchable RAFT agents, whose activity is regulated by acid or base addition during polymerization, allowing dispersity to be tailored block-by-block.[29]

Regarding the effect of polydispersity (PDI) on the morphology of block copolymer films, the available data demonstrate a diversity of observed effects. For example, in some studies [19,21,24,25,30,31], an increase in PDI leads to a shift in phase boundaries, whereas in other works [18,21,32], it results in the coexistence of two different morphologies. Even within the same class of copolymers, the observed trends can vary significantly depending on the synthesis conditions and sample composition.

Let us consider the effect of polydispersity on the morphology symmetry of styrene-based diblock copolymers with various (alkyl)acrylates, which are prone to microphase separation because they contain thermodynamically incompatible blocks [12,21,26,33,34]. Matyjaszewski et al. [12] on a polystyrene-block-poly(methyl acrylate) (PST-b-PMA) system with a narrow-dispersity PST block and a broad-dispersity PMA block (35 vol % PMA, $M_n^{PMA} = 18$ kDa) showed that increasing polydispersity up to 1.7 and imparting a symmetric MWD shape resulted in the stabilization of the metastable hexagonally perforated lamellar morphology; on a nearly symmetric composition (where PMA is the minority block), they showed that increasing the polydispersity of the PMA block from 1.15 to 1.55 induced a transition from a lamellar to a cylindrical morphology. Widin et al.[21] on a polystyrene-block-poly(methyl methacrylate) (PST-b-PMMA) system with a narrow-dispersity PST block and a broad-dispersity PMMA block (PDI = 1.7, $M_n = 29.2$ – 42.9 kDa, $f_{MMA} = 0.35$ – 0.63 , weak segregation $\chi N = 10.4$ – 14.8 at 140 °C) showed that increasing the polydispersity of the PMMA block shifted the phase boundaries (cylinder-to-lamellae transition toward higher f_{MMA}) and increased the domain spacing by 20–70% compared to narrow-dispersity analogues. Gentekos et al. [26] on a PST-b-PMMA system with varying MWD shape of the PST block ($M_n^{PST} = 50$ kDa, overall $M_n = 125$ kDa, PDI of PST block = 1.4) showed that changing the breadth and skew of the PST block MWD increased the domain spacing without altering the overall morphology or chemical composition. When the distribution was skewed toward low molecular weights, the domain spacing

increase reached 41% compared to a narrow-dispersity analogue. When skewed toward high molecular weights, the increase was about 15%.

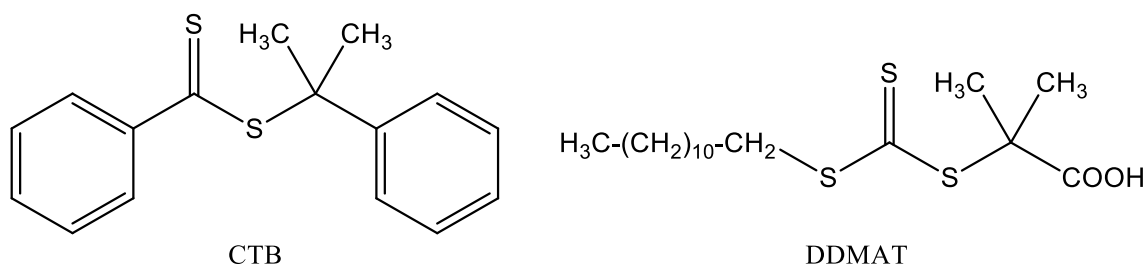
Thus, polydispersity becomes an additional key parameter governing the morphology of block copolymers and, consequently, the properties of materials derived from them. Controlling this parameter provides access to a broader range of morphologies; however, systematic experimental and theoretical research is necessary for the directed design of materials with predictable morphology.

The goal of this paper was to investigate the influence of PMMA-block polydispersity on the morphology of DCs films. For this purpose, DCs of approximately the same composition were synthesized by sequential two-stage RAFT polymerization using three PMMA samples with similar molecular weight and different polydispersity $M_w/M_n = 1.11, 1.21, 1.53$. The morphology of DCs was compared using a combination of small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

2 Experiment and Calculations

2.1 Materials

Monomers, methyl methacrylate (MMA), (99 %) and styrene (ST), (99 %) obtained from Aldrich were purified by vacuum distillation. Initiator, 2,2'-azobis(isobutyronitrile) (AIBN), (98 %, Sisco Research Laboratories) was purified by double recrystallization from methanol. RAFT agents, cumyl dithiobenzoate (CTB), (96 %, Sigma Aldrich Co.) and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT), (98 %, Sigma Aldrich Co.) were used as received. Solvents of AR grade were distilled before use.



2.2 Polymerization

All RAFT polymerizations were performed at 60 °C under vacuum in a Schlenk flask equipped with a magnetic stirrer and fitted with PTFE stopcocks. Prior to use, the flask was flamed under vacuum. A mixture of monomer, solutions of AIBN and RAFT agent in benzene was introduced in the Schlenk flask and degassed via three freeze-pump-thaw cycles to a residual pressure of 0.01 mbar. Monomer conversion was determined gravimetrically after drying the polymer to constant weight under vacuum.

2.3 Representative Synthesis of PMMA-RAFT agent

The PMMA-RAFT agent was prepared as follows: 3.75 ml of MMA (35 mmol), 3.84 mg of CTB (0.014 mmol), 4.63 mg (0.028 mmol) of AIBN, and 0.95 ml of benzene were introduced into the Schlenk flask. Polymerization was carried out at 60 °C for a specified time and then the polymer was twice recovered by precipitation from chloroform solution into a 10-fold excess of cold methanol, filtered off, dried under vacuum, and characterized. The preparation conditions and the molecular-weight characteristics for PMMA-RAFT agents obtained are collected in Table 1.

Table 1. Polymerization conditions of MMA at 60 °C and molecular-weight characteristics of prepared PMMA-RAFT agents

Sample	Concentration $\times 10^2$, mol/l			Time, h	q , %	$M_n^{\text{th}} \times 10^{-3}$	GPC		q_{CTA} , %
	CTB	DDMAT	AIBN				$M_n \times 10^{-3}$	PDI	
PMMA1	1.1	-	0.3	20	92	64.6	62.8	1.11	-
PMMA2	0.3	-	0.6	6	35	88.0	84.0	1.21	100
PMMA3	-	1.5	0.3	2	7	46.0	64.9	1.53	5

2.4 Representative Synthesis of DCs

DCs were synthesized by two-stage RAFT polymerization. In the first step, the PMMA block was prepared as described above. In a second step, ST was added to the desired amount of dried PMMA-RAFT agent, AIBN and benzene, degassed via three freeze-pump-thaw cycles to a residual pressure of 0.01 mbar and heated at 60 °C for a specified time. DCs were recovered by repeated dissolution in chloroform and precipitation in methanol and then dried in vacuum (residual pressure of 0.01 mbar) to constant weight. The preparation conditions and molecular-weight characteristics of DCs are presented in Table 2.

Table 2. Polymerization conditions of ST and molecular-weight characteristics of prepared DCs

Sample	Polymerization conditions ^{a)}			DCs				
	PMMA-RAFT agent	Time, h	<i>q</i> , %	NMR		GPC		<i>M_n</i> ^{b)} ×10 ⁻³
				Composition, mol %		<i>M_n</i> ×10 ⁻³	<i>PDI</i>	
				MMA	ST			
DC1	PMMA1	15	19	48	52	119.0	1.26	133
DC2	PMMA2	18	23	52	48	90.0	1.49	167
DC3	PMMA3	24	47	47	53	102.0	1.27	141

^{a)}[AIBN] = 2.6×10^{-3} mol/l, [PMMA] = 2.2×10^{-3} mol/l, [ST] = 7.17 mol/l, 60 °C

^{b)}The number-average molecular weight of DC was calculated as $M_n = M_n^{\text{PMMA}}(\text{GPC}) + \frac{M_n^{\text{PMMA}}(\text{GPC}) \times f_{\text{ST}} \times 104.15}{f_{\text{MMA}} \times 100.12}$, where $M_n^{\text{PMMA}}(\text{GPC})$ is the number-average molecular weight of PMMA block determined by GPC, 104.15 and 100.12 are the ST and MMA molecular weights, f_{ST} and f_{MMA} are mole fraction of ST and MMA units in the copolymer respectively.

2.5 The preparation of the DC films

The films of DC were prepared by depositing 5 wt.% solutions of the copolymer in toluene onto glass slides with a hydrophobic surface. The solvent was then evaporated in air at room temperature for 48 hours, and then annealing with a stepwise temperature increase every 4 hours: 50°C, 70°C, 100°C, and 130°C, which is above the glass transition temperature (T_g) of both PMMA (T_g = 115-118 °C [35]) and PST (T_g = 100-107 °C [36]). Upon reaching 160°C, the film was cooled in air at room temperature.

2.6 Methods

The molecular weight characteristics of polymers were determined by gel permeation chromatography (GPC) using Agilent 1200 Series Chromatography system equipped with an isocratic pump, refractive index detector, and

PLmixC column. Tetrahydrofuran (THF) was used as the eluent at 25 °C, and series of monodisperse PMMA or PST standards was used for calibration of PMMA and DC samples, respectively.

The ^1H NMR spectra were collected on an Avance TM 600 spectrometer from Bruker (Germany) with a proton operating frequency of 600.22 MHz. Chemical shifts were measured relative to the residual CHCl_3 signal in deuteriosolvent (7.28 ppm), and were then recalculated to tetramethylsilane. The accuracy of the chemical shift measurements was not worse than 0.001 ppm, and CDCl_3 was used as the solvent.

The morphology of the films was analyzed using TEM with a LEO 912ABOMEGA microscope. Ultrathin samples, approximately 100-200 nm in thickness, were prepared using a diamond knife on an Ultracut ultratome (Austria) at a speed of 1 $\mu\text{m/s}$. The film samples were then transferred to a 200-mesh copper grid with a carbon coating for analysis. SAXS experimental conditions: Rigaku diffractometer instrument, Moscow Institute of Physics and Technology [37]. The source of the X-ray radiation is a rotating copper anode. The wavelength is 1.5405 Å. The beam passing through the collimator hits the sample in the vacuum chamber. The X-ray radiation is detected by a position-sensitive detector. Calibration based on the angular values of the scattering vector modulus is performed using silver behenate [38].

3 Results and discussion

3.1 Synthesis of DCs with different PDI of PMMA blocks

The DCs were prepared via sequential two-stage RAFT polymerizations. In the first stage, PMMA blocks with different PDI were synthesized. For this purpose, we used both effective and ineffective low molecular weight CTAs, and varied the concentration of the effective CTA.

To obtain a narrowly dispersed PMMA block, RAFT polymerization of MMA was carried out in the presence of CTB at $[\text{AIBN}]/[\text{CTB}] = 1/3.7$. The theoretical average molecular weight (M_n^{th}) values were calculated based on the assumption that one molecule of CTA results in the controlled growth of one polymer chain, according to Equation (1):

$$M_n^{\text{th}} = M_{\text{CTA}} + \frac{q[\text{MMA}]_0 M_{\text{MMA}}}{[\text{CTA}]_0}, \quad (1)$$

where M_{CTA} , M_{MMA} are the molecular weights of the CTA and MMA, respectively; $[\text{CTA}]_0$ and $[\text{MMA}]_0$ are their initial concentrations, and q is monomer conversion.

The dependences of $M_n(\text{GPC})$, theoretical value M_n^{th} and M_w/M_n on MMA conversion are shown in Fig. 1. An analysis of the GPC data showed that the $M_n(\text{GPC})$ values for PMMA increase with increasing q and practically coincide with the theoretical M_n^{th} , calculated using Equation 1. The resulting polymers are characterized by low PDIs, slightly decreasing from 1.14 to 1.11 with increasing q from 6 to 92% (Fig. 1). This indicates the controlled nature of the polymerization reaction under the selected conditions. The results obtained are consistent with the data from Rizzardo et al. [39], who showed that CTB is the effective CTA for RAFT polymerization of MMA, and the latter occurs according to the pseudo-living mechanism with a chain transfer constant of $C_{\text{tr}} = 5.9$, which is significantly higher than 1.0.

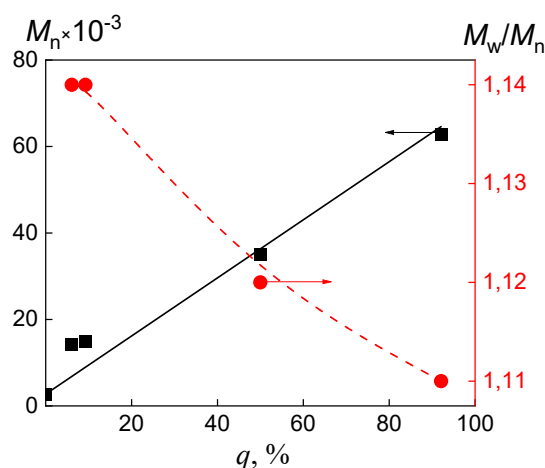


Fig. 1. The dependence of the M_n (black squares), M_n^{th} (black line), and M_w/M_n (red cycles) on conversion of MMA. [MMA] = 7.2 mol/l, [AIBN] = 0.3×10^{-2} mol/l, [CTB] = 1.1×10^{-2} mol/l, $T = 60^\circ\text{C}$.

To synthesize PMMA blocks with higher PDI compared to the narrowly dispersed sample, we tested the possibility of PDI controlling by adjusting the amount of CTA. A similar approach was earlier proposed by Matyjaszewski et al. in their work.^[12] The authors synthesized PST-*block*-PMA copolymers using activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP), and varied the PDI of the PMA block by adjusting the amount of copper catalyst. PMA with $M_w/M_n = 1.11$ was synthesized using 50 ppm of copper catalyst, and PMA with $M_w/M_n = 1.77$ was prepared using 5 ppm of copper catalyst.

We polymerized MMA with a smaller amount of CTB at [AIBN]/[CTB] = 1/0.5 and obtained PMMA homopolymers with M_w/M_n ranged from 1.27 to 1.21 (Fig. 2). CTB is almost completely consumed in the early stages of polymerization at $q = 10\%$. $M_n(\text{GPC})$ values for PMMA increase with q and practically coincide with the theoretical M_n^{th} , and PDI values slightly decrease with increase of conversion.

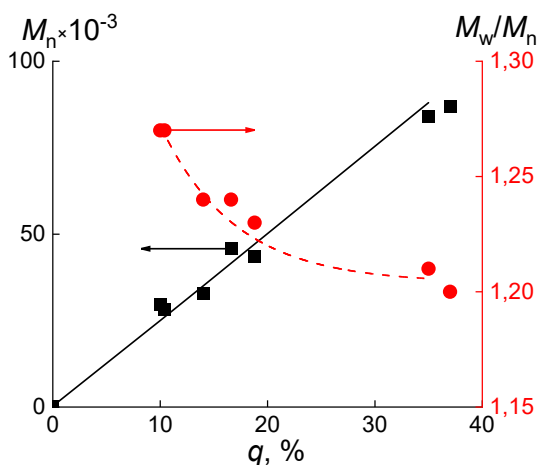


Fig. 2. The dependence of the M_n (black squares), M_n^{th} (black line), and M_w/M_n (red cycles) on conversion of MMA. [MMA] = 7.5 mol/l, [AIBN] = 0.6×10^{-2} mol/l, [CTB] = 0.3×10^{-2} mol/l, $T = 60^\circ\text{C}$.

The ^1H NMR spectrum of the PMMA obtained at [AIBN]/[CTB] = 1/0.5 and $q = 37\%$ is shown in Fig. 3. Four distinct signals are observed in the spectrum. The three protons of the methoxy group ($\text{CH}_3\text{-O-}$) resonate at 3.7–3.5 ppm (H1), while those of the methyl group ($\text{CH}_3\text{-}$) appear at 1.1–0.75 ppm (H2). The polymer backbone

protons give rise to the signal at 2.0–1.7 ppm (H3). The doublet at 7.9–7.95 ppm (H4) is assigned to the two ortho-protons of the phenyl ring in the Z-group of CTB. The number-average molecular weight of the PMMA was estimated using Equation (2):

$$M_{n\text{ PMMA}} = \frac{H1 \times 2}{3 \times H4} \times 100.12 \quad (2)$$

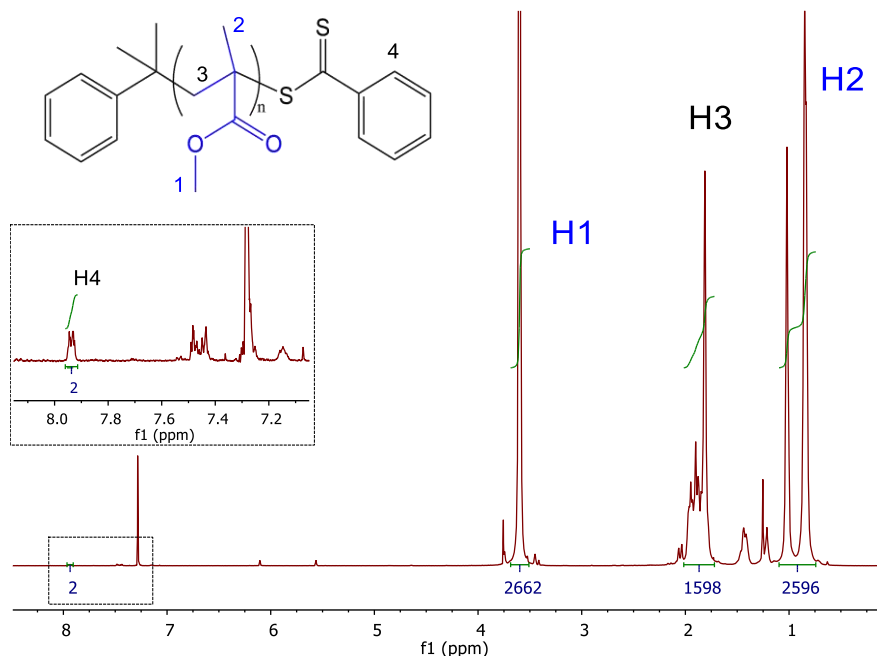


Fig. 3. ^1H -NMR spectrum of the PMMA prepared at $q = 37\%$. $[\text{MMA}] = 7.5\text{ mol/l}$, $[\text{AIBN}] = 0.6 \times 10^{-2}\text{ mol/l}$, $[\text{CTB}] = 0.3 \times 10^{-2}\text{ mol/l}$. $T = 60\text{ }^\circ\text{C}$. CDCl_3 was used as a solvent.

The values of M_n ($M_n^{\text{PMMA}}(\text{NMR}) = 89\text{ kDa}$) calculated by Equation 2 and determined by GPC ($M_n^{\text{PMMA}}(\text{GPC}) = 87\text{ kDa}$) are almost identical. These results indicate that the polymerization of MMA under these conditions proceeds by a pseudo-living mechanism. Thus, the PDI of PMMA can be controlled by adjusting the amount of CTB in RAFT polymerization of MMA.

The PMMA with higher $M_w/M_n = 1.53$ was prepared by polymerization of MMA in the presence of less effective CTA, DDMAT at $[\text{AIBN}]/[\text{DDMAT}] = 1/5$ (Table 1). When DDMAT was used as CTA, the molecular weights predicted for low conversions were higher than the theoretical M_n^{th} predicted by Equation (1). In these circumstances, the rate of consumption of CTA ($q(\text{DDMAT})$) is determined by Equation (3):

$$q(\text{DDMAT}) = \frac{M_n^{\text{th}}}{M_n(\text{GPC})} \quad (3)$$

Under our conditions, the chain transfer coefficient was determined from the slope of a plot of $\ln[\text{DDMAT}]$ versus $\ln[\text{MMA}]$ according to Equation (4)[39]:

$$C_{tr} = \frac{d(\ln[\text{DDMAT}])}{d(\ln[\text{MMA}])} \quad (4)$$

This analysis yielded a C_{tr} value of approximately 1.0 (Fig. 4). This means that DDMAT, even though it has a low C_{tr} , is still effective as a RAFT agent for MMA polymerization.

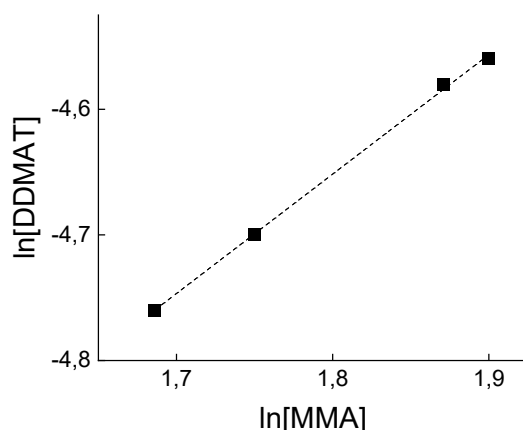


Fig. 4. Double log plots of DDMAT concentration vs MMA concentration for polymerization of MMA at conversion q about 9 %. $[AIBN] = 3.0 \times 10^{-2}$ mol/l, $T = 60$ °C. Correlation coefficient = 0.99893.

Thus, all these observations suggest that the polymerization of MMA with DDMAT proceeds in a living manner.

The PMMA samples with close M_n values but differing PDI shown in Table 1 were used for the synthesis of DCs. The MWD curves of these PMMA samples with PDI = 1.11, 1.21, and 1.53 are shown in Fig. 5.

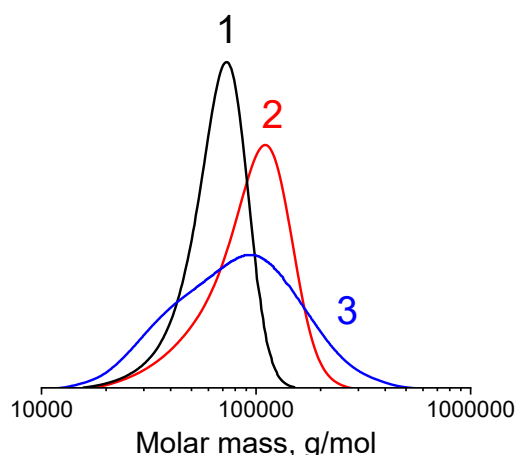


Fig. 5. The MWD curves of PMMA used for DCs synthesis: PMMA1 (1), PMMA2 (2), PMMA3 (3).

The increase in PDI from 1.11 to 1.53 was accompanied not only by a broadening of the MWD but also by a substantial change in its shape toward the predominance of longer macromolecules. As can be seen from (Fig. S1), the skewness indices S_n and S_w (Equation S1 and S2) of PMMA1 and PMMA2 are close to zero, which indicates that the shape of the MWDs is approximately symmetric. In contrast, PMMA3 exhibited positive skewness (S_n and $S_w > 0$), indicating a distribution skewed toward higher molecular weights.

Polymerization of ST was carried out at 60 °C at $[AIBN] = 2.6 \times 10^{-3}$ mol/l and $[PMMA] = 2.2 \times 10^{-3}$ mol/l for 15, 18 and 24 hs. The composition of the resulting DCs was determined by ^1H NMR spectroscopy. The ^1H NMR-spectrum of the DC2 in $CDCl_3$ (Fig. 6) exhibits six signals corresponding to protons of the functional groups. The first four signals (H1–H4) are attributed to the PMMA-RAFT agent fragments and have been described previously. The fifth signal at 7.25–6.9 ppm (H5) corresponds to the three protons in the meta- and para-positions of the phenyl ring of styrene units. The sixth signal at 6.9–6.3 ppm (H6) is assigned to the two protons in the ortho-

position of the phenyl ring of styrene. The content of MMA and ST in the copolymer (mol. %) was calculated using the Equation (5):

$$[MMA] = \frac{H_1}{H_1+H_5} \times 100\%; [ST] = \frac{H_5}{H_1+H_5} \times 100\% \quad (5)$$

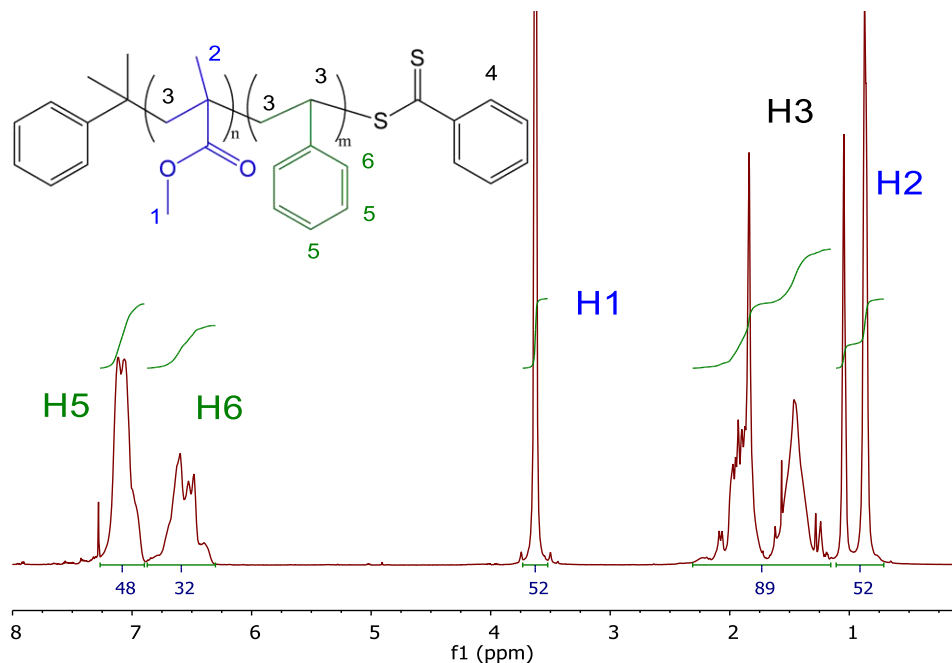


Fig. 6. ¹H-NMR spectrum of the DC2. CDCl₃ was used as a solvent.

The apparent MWD curves and average molar masses were estimated by GPC relative to PST standards. Accurate information on the molecular weight distribution of DCs cannot be obtained using GPC with a refractive index detector. The main reason for this is the approximately twofold difference in the instrument's sensitivity to PST and PMMA due to the difference in refractive index increments ($dn/dc(\text{PST}) = 0.195$ [40], $dn/dc(\text{PMMA}) = 0.083$ [41]). This difference in detector sensitivity results in an additional broadening of the calculated MWDs of copolymers due to composition inhomogeneity, which is typical to a greater or lesser extent for all copolymers, along with molecular weight inhomogeneity. In fact, composition inhomogeneity has been detected using critical chromatography technique in work [12] in PST-*block*-PMA copolymers synthesized by ARGET ATRP method. An additional factor affecting the correctness of the MWD determination is calibration uncertainty. It is known that in the GPC method, macromolecules are separated based on their hydrodynamic size. Block copolymers, which consist of incompatible blocks, can have a more compact size than homopolymers, that can lead to an underestimation of their apparent molar mass.

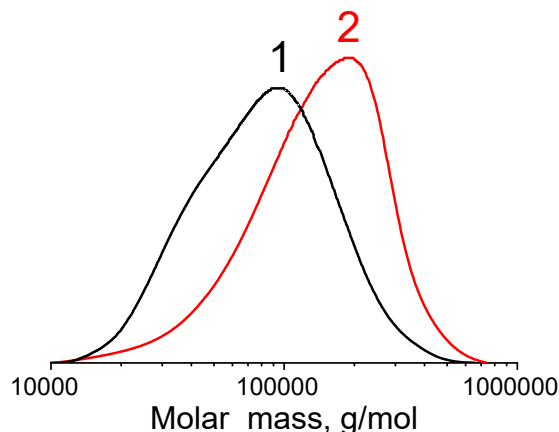


Fig. 7. The MWD curves of PMMA3 (1) and DC3 (2) obtained by GPC.

The obtained DCs are characterized by unimodal MWD curves with maxima shifted to higher molecular weight compared to the initial PMMA block. As an example, Fig. 7 shows the MWD curves for PMMA3 and DC3 obtained by polymerization of ST in the presence of PMMA3.

3.2 Investigation of the morphology of films made of DC

TEM and SAXS methods were used to experimentally study the morphology of films of synthesized samples DC1, DC2 and DC3.

Fig. 8 shows TEM images of films from DC1, DC2 and DC3, characterized by different PDI of the PMMA blocks. The film from DC1 (Fig. 8, a and b) has a pronounced lamellar structure with a period of about 60-74 nm. The period of lamellar structure L includes two full layers of MMA and ST units. At the edges of the film there is the lamellar morphology with junction points aligned along planar interfaces that reflect equivalent stretching of the copolymer blocks. While in the bulk of the film there is a slight lateral shift of the morphology boundaries. In fact, the same effect is also observed for the equimolar composition DCs of both ST with MMA and ST with butyl acrylate in works [34], [18]. A slight increase in the PDI of the PMMA block from 1.11 to 1.21 leads to a transition from lamellar morphology to a coexistence of two ordered phases. The first phase is PMMA matrix with spherical domains of PST dispersed in it ($\varnothing \sim 30$ nm). The second phase is lamellar microstructure with the period $L = 140$ -160 nm (Fig. 8, c). A further increase of the PDI of the PMMA block to 1.53 results in the formation of domains of PMMA blocks having a close to spherical shape with diameter from 10 to 60 nm, dispersed in the PST matrix (Fig. 8, d).

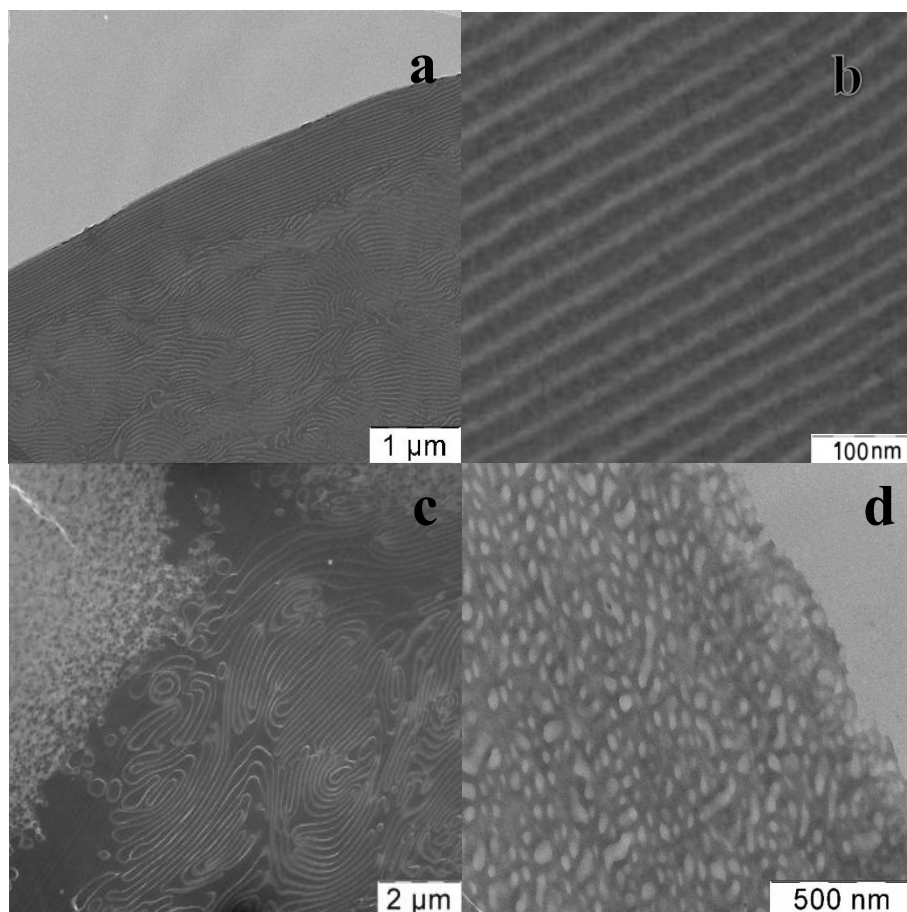


Fig. 8. TEM-images of unstained films from DC1 (a, b), DC2 (c) and DC3 (d). The dark regions in the TEM is PST.

The microstructure of the films was also examined using SAXS. Fig. 9 (curve 1) shows the scattering curve for the DC1 film on a double logarithmic scale, with the logarithm of the intensity on the y-axis and the modulus of the scattering vector (q) in inverse angstroms on the x-axis. The presence of several peaks can be seen from the SAXS profile. The main peak at $q = 8.8 \times 10^{-3} \text{ \AA}^{-1}$, as well as higher-order peaks at a ratio of $q \ 2 : 3 : 4$, indicate the lamellar morphology of the DC1 film. From the position of the main peak, we determined the value of the lamellar period $L = 67 \text{ nm}$. Thus, the visual data of the TEM and the results of the SAXS experiment are in good agreement.

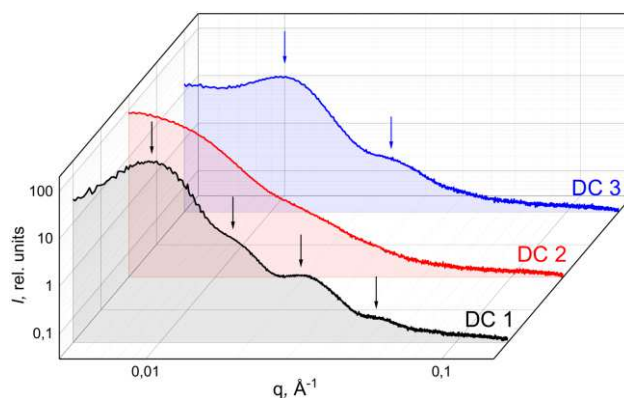


Fig. 9. The SAXS intensity profiles for films of DC1, DC2 and DC3 on a double logarithmic scale.

In contrast to the well-ordered lamellar microstructure of the film of DC1 with PDI of PMMA block = 1.11, we were unable to detect any ordered domain structure in the films from DC2 and DC3 containing more widely

dispersed PMMA blocks. The SAXS profile for the DC2 film with two-phase morphology (spheres and lamellae) (Fig. 9, curve 2) shows one wide peak at $q = 1.5 \times 10^{-2} \text{ \AA}^{-1}$. To interpret the result obtained, the scattering curve was modeled (Fig. 10, a) and the structure factor was determined (Fig. 10, b). The analysis of the structure factor showed that spherical aggregates predominate in the microstructure of the film, and the lamellar structure is represented locally. The position of the peak $q = 1.5 \times 10^{-2} \text{ \AA}^{-1}$ corresponds to disordered spherical aggregates with a diameter of 28 nm.

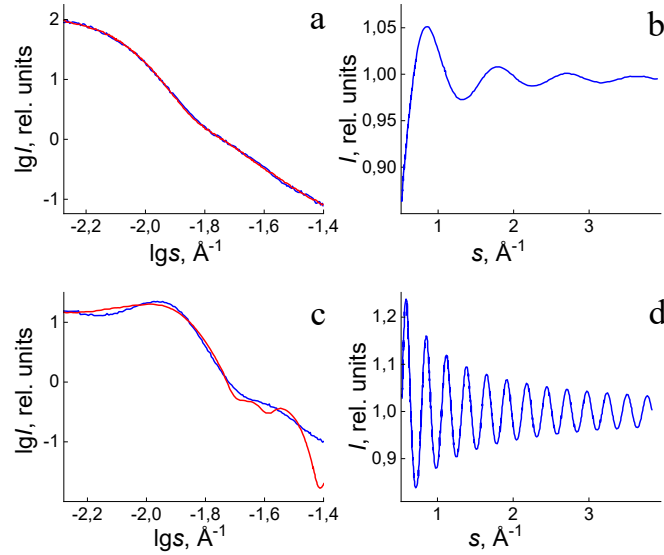


Fig. 10. Modeling of the scattering curve (a, c) and the structure factor (b, d) for films from DC2 (a, b) and DC3 (c, d). Experimental data are shown in blue, and the modeled curves in red. The simulation was performed using the MIXTURE [42] and SASPLOT [43] programs.

Two peaks are observed on the scattering profile for the DC3 film (Fig. 9, curve 3). The maximum at $q = 1.08 \times 10^{-2} \text{ \AA}^{-1}$ corresponds to the scattering from spherical aggregates with an average diameter of $\varnothing = 58 \text{ nm}$. Modeling the size distribution taking into account the structural factor (Fig. 10, c, d) showed that the volume fraction of spherical particles in the microstructure of the film is approximately 98%.

Table 3. Comparison of the results of the study of film morphology using TEM and SAXS

Films	Morphology type	$L, \text{ nm}$	
		TEM	SAXS ^{a)}
DC1	lamellar	60-74	67
DC2	spherical and lamellar	40 and 150	28 and 120
DC3	spherical	20-60	58

^{a)} The distance between the domains is measured as $2\pi/q$.

The observed deviation of the calculated scattering curve from the experimental one can be explained by the nonspherical shapes of the globules and interference between particles of different shapes (the latter cannot be taken into account in the calculation due to ambiguity). We compared the sizes of spherical domains and lamellar periods obtained from the analysis of TEM images and SAXS intensity curves (Table 3). It can be seen that the numerical values of the sizes of spherical domains, as well as lamellar periods, determined by both methods,

practically coincide. However, the SAXS method is preferable because it provides more complete information about morphology, unlike local TEM data.

Thus, as the polydispersity of the PMMA block increases, we observe a progressive shift from a lamellar morphology to a spherical one. This trend toward higher interfacial curvature was predicted [44] and experimentally confirmed [31]. The explanation lies in the redistribution of chain lengths: long chains are extended into the centers of domains while short chains localize near the interface, reducing the entropic stretching energy of the polydisperse block and causing the interface to curve toward it. Moreover, such chain arrangement, together with the ability of highly asymmetric chains to pull out from the interface entirely and act as an «effective homopolymer» (as defined by Widin et al [21].), leads to an increase in the lamellar period [21,26,30,31]. In our case the lamellar period increases from 67 nm for the narrow-dispersity sample to 120 nm for the sample with PDI = 1.21.

Matsen predicted that the coexistence of two phases results from fractionation of the MWD [45]. This coexistence was experimentally observed by Widin [21] and Schmitt [32]. In our sample at PDI = 1.21 the minority lamellar phase is formed by diblock copolymers with compositions close to equimolar (symmetric chains), while the remaining majority of chains segregate into the spherical phase.

3.3 The determination of Flory-Huggins interaction parameter χ between PMMA and PST using the lamellar structure the period in DC films

The Flory-Huggins interaction parameter χ between PST and PMMA has been the subject of several studies over the last 6 decades [33,46–48]. Surprisingly or not, the reported values of the interaction parameter vary from 0.011 up to 0.0645 as measured by a wide variety of techniques.

We have used the SAXS observed lamellar period to calculate the Flory-Huggins interaction parameter χ . Based on the theory predicted by Semenov A.N. for a hypothetical model monodisperse block copolymer melt^[6] the χ can be determined using the following Equation 6:

$$\chi = \left(\frac{L}{c \times a \times N^{(2/3)}} \right)^6, \quad (6)$$

where L is period of the microphase separation, a is the length of the Kuhn segments of each of the blocks, N is the number of segments in each of the blocks, and c is a coefficient depending on the type of microphase separation structure.

For the period of the lamellar structure $c = 8(3/\pi^2)^{1/3}$, and the Flory-Huggins parameter is determined by Equation 7:

$$\chi_{PMMA/PST} = \left(\frac{L}{5.4 \times a \times N^{(2/3)}} \right)^6, \quad (7)$$

where $a = 0.7$ nm,^[33] and the total number of Kuhn segment is calculated as follows:

$$N = N_{PMMA} + N_{PST} = \frac{M_{nPMMA}}{S_{PMMA} \times M_{mMMA}} + \frac{M_{nPST}}{S_{PST} \times M_{mST}} = \frac{62800}{6 \times 100.12} + \frac{68033}{7.9 \times 104.15} = 187, \quad (8)$$

here the number of monomeric units in the PST segment is $S_{PST} = 7.9$ [49]. The N_{PST} was calculated as $N_{PST} = \frac{M_{nPMMA} \times f_{ST}}{f_{MMA} \times 100.12}$, where M_{nPMMA} is the number-average molecular weight of PMMA block, 100.12 is the molecular weight of MMA, f_{ST} and f_{MMA} are mole fraction of ST and MMA units in the copolymer.

Thus,
$$\chi_{PMMA/PST} = \left(\frac{67}{5.4 \times 0.7 \times 187^{(2/3)}} \right)^6 = 0.023$$

The value of the Flory-Huggins parameter obtained by processing the lamellar structure is in good agreement with the experimental value of the Flory-Huggins parameter $\chi(\text{PMMA/PST}) = 3.0 \times 10^{-3}$, determined by the light scattering method at 30 °C for binary mixtures of PST and PMMA with molecular weights close to ours [46].

The effect of the increase of PMMA block PDI from 1.11 to 1.53 of on the morphology of DC films observed here can be explained by the segregation of DC chains according to PMMA block lengths. The copolymers with the shortest PMMA blocks are likely to progressively dissolve in the microdomains of PST. Theoretical modeling of similar polydisperse copolymers indeed predicts that, short chains have smaller segregation strength χN and are therefore relatively well mixed throughout the system [50]. The DC with the longest PMMA blocks will determine the morphology of the DC film, in which PMMA spherical domains are dispersed in PST matrix. DC chains of intermediate PMMA block lengths are concentrated at DC domain interfaces and cause curvature of the interface surface even at symmetrical compositions. Such segregation of chains according to their length within microdomains is indeed also predicted by theory [50].

4 Conclusions

Thus, the width and symmetry of the molecular weight distribution of the PMMA block is important parameter that affects the microphase separation. The results show that DC of equimolar composition with narrow MWD of the PMMA block prepared by RAFT polymerization at $[\text{AIBN}]/[\text{CTB}] = 1/3.7$ ($M_w/M_n = 1.11$) contribute to the stabilization of the lamellar morphology. The slight increase in the PDI of the PMMA block (implemented by obtaining the PMMA block by RAFT polymerization at $[\text{AIBN}]/[\text{CTB}] = 1/0.5$) up to $M_w/M_n = 1.21$ leads to the system consisting of two ordered phases: the first phase is PMMA matrix with PST spherical domains, and the second phase is PST matrix with PMMA lamellae. The increase in the PDI to 1.53 (implemented by obtaining the PMMA block by RAFT polymerization in the presence of less effective RAFT agent) leads to transition in the morphology to spherical one. The results point to the importance of controlling both the width and symmetry of the molecular weight distribution as a potential route to the customized synthesis of microstructures with specific topological properties that may be of future technological interest.

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