Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2022, **32**, 241–243

Mendeleev Communications

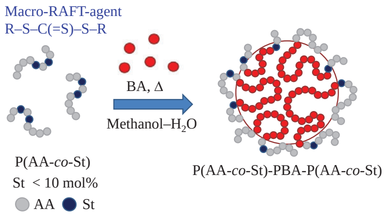
Styrene–acrylic acid copolymers as new stabilizers of dispersion RAFT polymerization of butyl acrylate

**Natalia S. Serkhacheva,*[a] Kseniya S. Galynskaya,[a] Nikolay I. Prokopov,[a] Kseniya O. Mineeva,[b]
Anna V. Plutalova[b] and Elena V. Chernikova*[b]**

[a] *M. V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University, 119571 Moscow, Russian Federation. E-mail: natalia-serkhacheva@yandex.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: chernikova_elena@mail.ru*

DOI: 10.1016/j.mencom.2022.03.029

The RAFT-based copolymers of acrylic acid and styrene may be successfully used as stabilizers of dispersion polymerization of butyl acrylate by providing the formation of stable block copolymer dispersion.

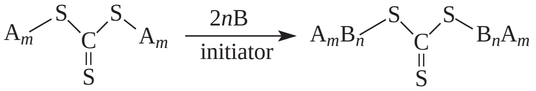


Keywords: reversible addition–fragmentation chain transfer (RAFT) polymerization, dispersion polymerization, polymerization-induced self-assembly, block copolymers.

Butyl acrylate copolymers of various microstructures containing styrene and acrylic acid units are promising adsorbents, paint and lacquer materials including coatings, pH responsive nanocapsules, *etc.*[1] These copolymers are traditionally produced by emulsion radical polymerization which is an environment friendly technology. However, the emulsifiers used for stabilization of the prepared polymer dispersions are easily eluted, and the system loses its colloidal stability. To prevent this, the covalent binding of emulsifier or stabilizer with polymeric chain is required. In some cases, the use of persulfate based radical initiator can solve this problem by electrostatic stabilization due to terminal sulfate groups derived from the initiator.[2] Also, polymerizable surfactants may be utilized.[3]

Recently, it was proposed to use solvophilic macroinitiators and polymeric transfer agents to synthesize the polymer dispersions of desirable morphology with narrow molecular weight distribution *via* heterophase (emulsion or dispersion) polymerization of solvophobic monomer(s). This approach known as polymerization-induced self-assembly (PISA) results in the *in situ* formation of block copolymers of various architectures through radical reversible-deactivation mechanism.[4–6] In our previous works we utilized various hydrophilic and amphiphilic copolymers containing trithiocarbonate group within the macromolecule to polymerize *n*-butyl acrylate (BA) in emulsion or miniemulsion.[7,8] These compounds include polyacrylic acid and its copolymers with styrenesulfonic acid sodium salt, *N*-isopropylacrylamide and fluoroalkyl acrylates. Note that our trials to perform dispersion polymerization of butyl acrylate were limited mainly to the use of hydrophilic polyacrylic acid and its copolymer with *N*-isopropylacrylamide.[8]

Dispersion RAFT polymerization of monomer B initiated by radical initiator and mediated by polymeric symmetrical trithiocarbonates A_m–SC(=S)S–A_m results mainly in the formation of triblock copolymer A_mB_n–SC(=S)S–B_nA_m (*m* and *n* indicate the degree of polymerization).[7]



The block copolymer contains terminal solvophilic blocks A_m and solvophobic block B_n growing throughout the reaction and one trithiocarbonate group within the chain. After reaching the critical length of the solvophobic block, the block copolymers form micelles. The incorporation of the propagating radical into the micellar core, which may also contain a certain amount of hydrophobic monomers, launches the nucleation of the polymeric particles, thus, the sequence of reversible chain transfer reactions continues in the polymeric particles.[8]

Here we report on the use of amphiphilic copolymers of styrene and acrylic acid, containing trithiocarbonate group within the chain, in the dispersion polymerization of butyl acrylate. Chain composition and microstructure determine the properties of styrene and acrylic acid copolymers in films and solutions.[9] Hence, we can assume that these factors, which are governed by the polymerization conditions, also affect the stabilizing properties of the copolymers.

Random copolymers of acrylic acid (AA) and styrene containing trithiocarbonate group within the chain and excess of AA units were synthesized by RAFT polymerization in DMF (r_{AA} = 0.08 and r_{St} = 0.85)[10] and 1,4-dioxane (r_{AA} = 0.01 and r_{St} = 0.26).[11,†] Upon completion of the reaction, the copolymers were purified *via* dialysis and lyophilized. Their designation, molar mass characteristics and composition are given in Table 1.

[†] Random copolymers of AA and styrene were synthesized as follows. Dibenzyl trithiocarbonate (BTC) (0.1 mol dm^{-3}) and azobisisobutyronitrile (AIBN) (10^{-3} mol dm^{-3}) were dissolved in the mixture of monomers and the solvent (1 : 1, v/v). The reaction mixture was polymerized under nitrogen atmosphere at 80 °C up to 80–90% monomer conversion.

Table 1 Macro-RAFT agents and their characteristics.

Copolymer	AA : styrene molar ratio in feed	Solvent	M_n/ g mol^{-1}	*Đ*	AA molar part in the copolymer
C1	95 : 5	1,4-dioxane	5800	1.11	0.91
C2	95 : 5	DMF	4700	1.10	0.89
C3	90 : 10	1,4-dioxane	4300	1.20	0.84
C4	90 : 10	DMF	5300	1.19	0.82

All the copolymers (C1–C4) are soluble in DMF, methanol and ethanol. Their diluted solutions have been analyzed by dynamic light scattering (DLS).[‡] The number average diameters (D_n) of the particles in the diluted solutions of the above-mentioned solvents are 1.5–2.0 nm, which correspond to the individual macromolecules. However, we failed to perform RAFT dispersion polymerization of BA mediated by C1–C4 in pure alcohols, which are the bad solvents for poly(*n*-butyl acrylate).

Copolymers C3 and C4 are insoluble in water and water–alcohol mixtures, which represent the bad solvents for poly(*n*-butyl acrylate). Therefore, the styrene units content exceeding 15 mol% in the amphiphilic copolymer with AA disables the choice between the poor solvent for propagating poly(*n*-butyl acrylate) and the good solvent for C3 and C4. Thus, RAFT dispersion polymerization occurs.

Opposite situation has been noticed for C1 and C2. Both copolymers are partly soluble in water and soluble in water–alcohol mixtures. The dependence of D_n on water content in water–methanol mixture is presented in Figure 1. As can be seen, the curves are S-chaped; sharp increase of D_n is observed at ~20 vol% of water for C1 and ~10 vol% of water for C2. This difference can be caused by distinct chain microstructure, inasmuch as the content of hydrophobic styrene in the copolymers C1 and C2 is similar. Thus, these media were chosen to carry out the dispersion polymerization of butyl acrylate.

Dispersion polymerization of BA was performed in water–methanol mixture under batch and semibatch conditions. In the first case, C1 or C2 and AIBN were dissolved in dispersion medium (methanol–water mixture, 10 or 20 vol% of water). Then BA was rapidly added under nitrogen atmosphere, maintaining monomer to dispersion medium ratio of 1 : 5 (v/v). In the second case, BA was added under nitrogen atmosphere in two steps: 10 vol% of BA at the beginning of the reaction, then after 5 min the rest amount of the monomer was loaded using a BYZ-810 syringe pump with BA dosing rate of 0.1 ml min^{-1}. The final volume ratio of monomer to dispersion medium, containing 20 vol% of water, varied from 1 : 5 to 1 : 10. Polymerization was carried out with continuous stirring at 65 °C.

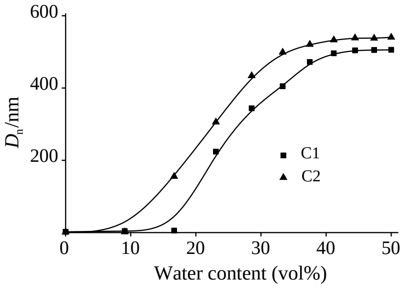


Figure 1 Dependence of D_n of copolymers C1 and C2 on water content in water–methanol mixture. Copolymer concentration 1 wt%.

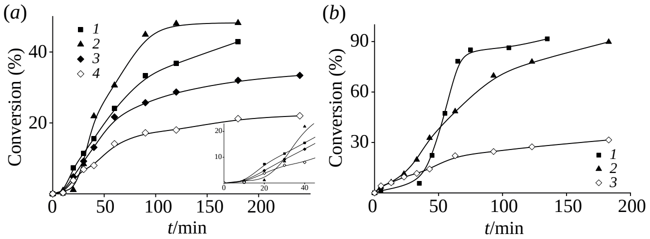


Figure 2 Monomer conversion *vs.* time in (*a*) batch and (*b*) semibatch dispersion polymerization of BA mediated by C1 and C2 at 65 °C, [C1] = = [C2] = 10^{-3} mol dm^{-3} in (*a*) (*1, 2*) methanol : water (80 : 20, v/v) and (*3, 4*) (90 : 10, v/v); butyl acrylate : medium (1 : 5, v/v); [AIBN] is (*1*) 4×10^{-3}, (*2, 3*) 6×10^{-3} and (*4*) 9×10^{-3} mol dm^{-3}; (*1–3*) C1, (*4*) C2 and (*b*) methanol : water (80 : 20, v/v); (*1*) butyl acrylate : medium (1 : 5, v/v) and (*2, 3*) (1 : 10, v/v); [AIBN] is (*1*) 8×10^{-3} and (*2, 3*) 10×10^{-3} mol dm^{-3}; (*1, 2*) C1 and (*3*) C2.

Figure 2 presents the kinetics of batch and semibatch RAFT dispersion polymerization of butyl acrylate. All the kinetic curves are S-shaped and reveal the short induction period, which corresponds to the term of formation of polymeric-monomeric particles, such profile is typical for the dispersion polymerization.[§] The increase of water content results in unexpected increase of the induction period and to the rise in the polymerization rate [Figure 2(*a*) (curves *2, 3*)]. The decrease of initiator concentration shortens the induction period and increases the initial polymerization rate [Figure 2(*a*) (insert) (curves *1*, *2*)]. The use of C2 causes the lower monomer conversion in comparison with C1 [Figure 2(*a*) (curves *3, 4*)], which may be caused by the different stabilizing ability of C1 and C2.

To increase the monomer conversion, the semibatch process was performed.[12] In this case, the extending of the duration of the induction period [Figure 2(*b*) (curve *1*)] comparing with the batch process [Figure 2(*a*) (curve *2*)] is due to the reduction of the initial monomer concentration. At the same time, the slow monomer loading into the reaction allows one to achieve the higher polymerization rate after the completion of polymeric particles formation. The twofold increase of the monomer/medium volume ratio (from 1 : 5 to 1 : 10) results in the rapid particle formation [Figure 2(*b*) (curve *2*)] caused by detioration of the thermodynamic quality of the medium with regard to the polymer. However, in the case of C2 we failed to improve the process.

It may be assumed that C1 and C2 exhibit different efficiency and stabilizing ability in RAFT dispersion polymerization of butyl acrylate. The particle size distributions for dispersions obtained in the presence of C1 are unimodal and D_n varies from 36 to 135 nm depending on the polymerization conditions. In contrast, using C2 results in the values of D_n ~2 μm.

To confirm the formation of triblock copolymers, the molecular weight distribution of the polymers formed throughout reaction was analyzed by size exclusion chromatography (SEC).[¶] As an example, Figure 3 depicts the SEC curves of the synthesized polymers in batch [(*a*) and (*b*)] and semibatch [(*c*) and (*d*)] processes. In all the ivestigated systems the resulting polymer was ‘living’ and its molar mass (MM) increased with the progress of the monomer conversion. However, in both batch and semibatch dispersion polymerization in the presence of C2 the RAFT mechanism was violated.

[‡] DLS analysis of the diluted solutions of macro-RAFT agents in methanol was performed using the Malvern Zetasizer Nano-ZS instrument equipped with He-Ne laser (λ = 633 nm, at 173 °C).

[§] The total monomer conversion was determined by gravimetry taking into account the weight of C1 or C2 in the sample.

[¶] The measurements were performed in DMF containing 0.1 wt% of LiBr at 50 °C using the Polymer Laboratories GPC-120 chromatograph with a refractive index detector and two PLgel 5 μm MIXED B columns for the MM range from 5×10^2 to 1×10^7 g mol^{-1}. The SEC system was calibrated using narrow-dispersed linear poly(methyl methacrylate) standards.

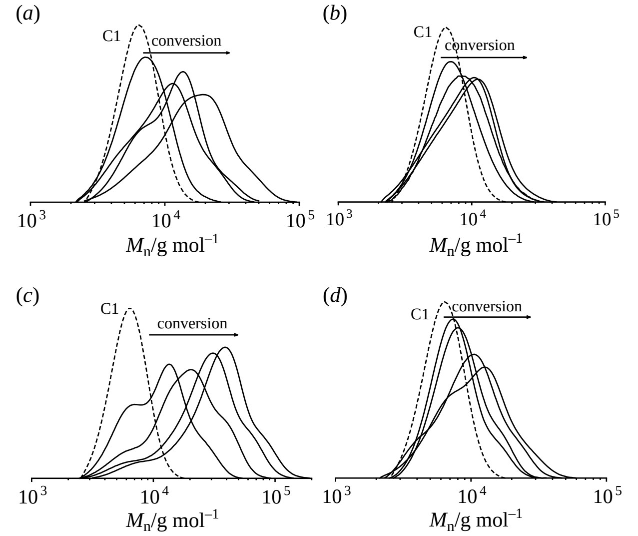


Figure 3 The SEC curves normalized by the unit area for the polymers formed at various monomer conversions during BA dispersion polymerization mediated by C1 at 65 °C, [C1] = 10^{-3} mol dm^{-3}, butyl acrylate : medium *(a–c)* (1 : 5) and *(d)* (1 : 10, v/v), methanol : water *(a, c, d)* (80 : 20) and *(b)* (90 : 10, v/v), [AIBN] *(a, b)* 6 × 10^{-3}, *(c)* 8 × 10^{-3} and *(d)* 10 × 10^{-3} mol dm^{-3}.

The estimation of number-average MM (M_n) of the grown polymer by separation of the peaks on the SEC curves stands in favour of this assumption. Figure 4(*a*) demonstrates the typical SEC curves of the grown polymers after separation of the peaks from the chromatograms given in Figure 3(*a*). As can be seen, the SEC curves of the grown polymers shift towards higher MM throughout polymerization in accordance with RAFT mechanism. The M_n of the grown polymer increases with the progress in the monomer conversion [Figure 4(*b*)] and dispersity *Đ* is in the range 1.14–1.28.

In conclusion, we have demonstrated for the first time that formed in 1,4-dioxane RAFT-based copolymers of acrylic acid and styrene containing trithiocarbonate group (< 10 mol%) within the chain may be successfully used as stabilizers of dispersion polymerization of butyl acrylate. This approach may be also extended to other RAFT-based copolymers to obtain the stable dispersions with desired functionalities.

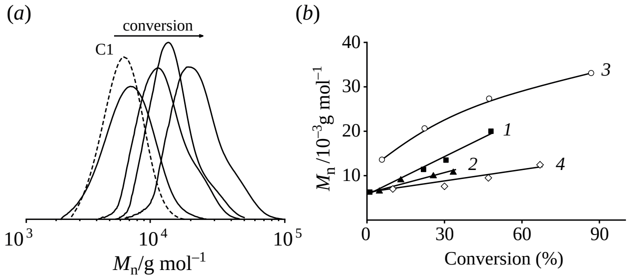


Figure 4 (*a*) The SEC curves for the grown polymers formed at various monomer conversions during BA dispersion polymerization initiated by AIBN (6 × 10^{-3} mol dm^{-3}) and mediated by C1 (10^{-3} mol dm^{-3}) at 65 °C, butyl acrylate : medium (1 : 5, v/v), methanol : water (80 : 20, v/v). (*b*) Dependences of M_n on the monomer conversion for grown polymers formed during BA dispersion polymerization mediated by C1. The curves numbers correspond to the systems indicated in Figure 3: (*1*) – *(a)*, (*2*) – (*b*), (*3*) – (*c*) and (*4*) – (*d*).

This work was performed under financial support of RFBR (grant no. 19-33-90096).

References

1 J. Zhou, H. Wang, L. Zhang and J. Ma, *Polym. Int.*, 2014, **63**, 2098.
2 T. Ngai and C. Wu, *Langmuir*, 2005, **21**, 8520.
3 M. Summers and J. Eastoe, *Adv. Colloid Interface Sci.*, 2003, **100–102**, 137.
4 E. J. Cornel, J. Jiang, S. Chen and J. Du, *CCS Chem.*, 2020, **2**, 2104.
5 F. D'Agosto, J. Rieger and M. Lansalot, *Angew. Chem., Int. Ed.*, 2020, **59**, 8368.
6 *Macromolecular Self-Assembly*, eds. L. Billon and O. Borisov, John Wiley & Sons, Inc., Hoboken, NJ, 2016.
7 N. S. Serkhacheva, N. I. Prokopov, E. V. Chernikova, E. Y. Kozhunova, I. O. Lebedeva and O. V. Borisov, *Polym. Int.*, 2019, **68**, 1303.
8 N. S. Serkhacheva, A. V. Plutalova, E. Y. Kozhunova, N. I. Prokopov and E. V. Chernikova, *Polym. Sci., Ser. B*, 2018, **60**, 204 (*Vysokomol. Soedin., Ser. B*, 2018, **60**, 156).
9 S.-L. Chen, P.-F. Shi and W.-Q. Zhang, *Chin. J. Polym. Sci.*, 2017, **35**, 455.
10 E. V. Chernikova, S. D. Zaitsev, A. V. Plutalova, K. O. Mineeva, O. S. Zotova and D. V. Vishnevetsky, *RSC Adv.*, 2018, **8**, 14300.
11 L. Couvreur, B. Charleux, O. Guerret and S. Magnet, *Macromol. Chem. Phys.*, 2003, **204**, 2055.
12 N. S. Serkhacheva, E. V. Chernikova, M. S. Balashov, N. I. Prokopov and R. V. Toms, *Mendeleev Commun.*, 2020, **30**, 731.

Received: 9th August 2021; Com. 21/6638