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Controlling monomer sequence distribution in RAFT polymerization of styrene and acrylic acid

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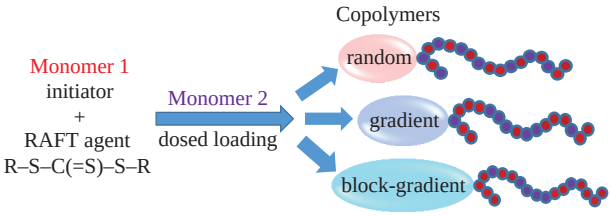
Continuous and semicontinuous RAFT copolymerization was first applied to synthesize well-defined copolymers of styrene and acrylic acid. The obtained copolymers have a different monomer sequence distribution due to different ways of adding acrylic acid to the reaction medium.



Keywords: reversible addition–fragmentation chain-transfer (RAFT) polymerization, copolymerization, random copolymers, block copolymers, gradient copolymers.

Living ionic polymerization and reversible-deactivation radical polymerization (RDRP) are versatile tools for constructing macromolecules.[1,2] Both techniques provide control of the chain architecture, molecular weight and molecular weight distribution, as well as end-group and side-group functionalities. The microstructure of polymers, *i.e.*, the tacticity of homopolymers and the monomer sequence of copolymers, is another essential factor that can be controlled. Random, alternating, gradient and block copolymers vary significantly in their macroscopic properties[3,4] such as glass transition temperature, elastic modulus and ability to self-assembly. Thus, a directed change in the properties of copolymers of the same chemical composition by controlling the sequence of their monomers is an urgent task of polymer science.

In radical polymerization, the reactivity and feed ratio of the monomers strictly determine both the copolymer composition and the monomer sequence distribution.[5] In general, the monomer reactivity ratio is a constant value for a given pair of monomers. Thus, depending on the chemical nature of the monomers, *i.e.*, their reactivity ratio, it is possible to synthesize either alternating or random copolymers in the case of conventional radical copolymerization and either alternating or random or gradient copolymers in the case of RDRP.[6,7] The bootstrap effect (or the effect of selective solvation of the active center) observed in the copolymerization of polar and nonpolar monomers, heterophase copolymerization and copolymerization of monomers capable of H-bonding or other interactions are exceptions to the general rule.[8] However, these exceptions usually lead to a jump in the monomer reactivity depending on the reaction conditions. Fine-tuning of the copolymer microstructure is unattainable for conventional radical polymerization. However, in RDRP, this can be achieved by the precise addition of monomers in the copolymerization at a given rate. The latter approach has been used in the reversible addition–fragmentation chain-transfer (RAFT) copolymerization of acrylonitrile with *N*-isopropylacrylamide or acrylic acid to control thermooxidative stabilization of the copolymers,[9,10] as well as in the nitroxide-mediated copolymerization of styrene with acrylic acid using mono- and bifunctional macronitroxides based on polyacrylic acid, which is formed *in situ*, to prepare diblock and triblock gradient copolymers, poly(acrylic acid)-*block*-poly(styrene-*grad*-acrylic acid) and poly(acrylic acid)-*block*-poly(styrene-*grad*-acrylic acid)-*block*-poly(acrylic acid), respectively.[11]

We recently described the batch RAFT copolymerization of styrene and acrylic acid in polar and low polar solvents mediated by trithiocarbonates and dithiobenzoates.[12–14] The monomer reactivity was shown to depend on the solvent polarity and the polarity of the polymeric RAFT agent. In this paper, we report the first attempt at fine-tuning the copolymer microstructure using various modes of introducing acrylic acid (Table 1) into the RAFT copolymerization with styrene in the low-polarity solvent 1,4-dioxane in the presence of dibenzyl trithiocarbonate (BTC).[†] In all syntheses, the amounts of initiator and RAFT agent are calculated assuming

Table 1 Loading methods of acrylic acid in RAFT copolymerization with styrene.

Entry	Acrylic acid loading		Note
	Method	Rate/ml h^{-1}	
1	–	–	Homopolymerization of styrene
2	Simultaneous	–	Batch copolymerization
3	Continuous	1.3	Acrylic acid is added for 8 h
4	Semicontinuous	2.3	Acrylic acid is added during the first 4 h of the reaction
5	Semicontinuous	0.7	Half of the initial amount of acrylic acid is added for 8 h
6	Semicontinuous	2.3	Acrylic acid is added during the last 4 h of the reaction
7	Semicontinuous	2.3	Acrylic acid is added after 2 h of styrene polymerization during the next 4 h of the reaction

[†] The polymerization was carried out in a 100 ml three-necked flask equipped with an overhead device with an anchor-type stirrer. A solution

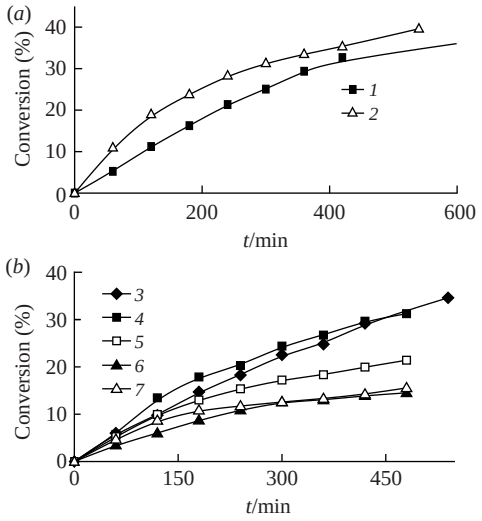


Figure 1 (*a*) Dependence of the total conversion of monomers (in relation to the monomer introduced at the moment) on the polymerization time in (*1*) RAFT homopolymerization of styrene and (*2*) RAFT copolymerization of styrene with acrylic acid in 1,4-dioxane at 80 °C. (*b*) Effect of (*3*)–(*7*) loading methods of acrylic acid in the RAFT copolymerization with styrene on the total conversion of monomers. The curve number corresponds to the entry in Table 1.

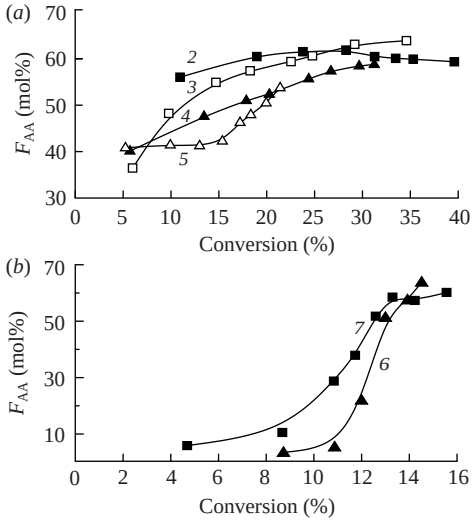


Figure 2 (*a*) Dependence of the average molar fraction of acrylic acid in the copolymer (F_{AA}) on the monomer conversion for copolymers formed in the RAFT copolymerization of styrene and acrylic acid using the methods of loading acrylic acid into the reaction described in Table 1, entries 2–5. (*b*) The same dependence for the acrylic acid loading methods described in Table 1, entries 6 and 7. The curve number corresponds to the entry in Table 1.

that the styrene/acrylic acid ratio is equimolar and the volumes of solvent and monomers are equal. However, according to the chosen synthetic procedure (continuous and semicontinuous), the reaction volume gradually increases due to the continuous loading of acrylic acid, which leads to a shift in reactant concentrations.

Figure 1 presents the dependence of the total conversion of monomers (in relation to the monomer introduced at the moment) on the polymerization time for the experiments given in Table 1. The addition of an equimolar amount of acrylic acid to styrene leads to an increase in the polymerization rate due to the high probability that the acrylic acid active unit is located at the end of the propagating radical in accordance with the ratio of monomer reactivity in 1,4-dioxane [Figure 1(*a*)].[14] An increase in the rate of loading of acrylic acid into the reaction, *i.e.*, an increase in its concentration, results in a similar effect [Figure 1(*b*)].

In 1,4-dioxane, both monomers preferentially react with the propagating radical of the other monomer, since the copolymerization constants for acrylic acid and styrene are $r_{AA} = 0.23$ and $r_{St} = 0.32$, respectively.[14] Thus, when the molar fraction of acrylic acid in the monomer feed is lower or higher than 46.9%, the acrylic acid content in the copolymer will be respectively higher or lower than in the monomer feed. The copolymer composition was analyzed by Fourier transform infrared (FTIR) spectroscopy (Figure 2).[‡] In the batch copolymerization, the copolymer composition remains almost constant throughout the entire copolymerization [Figure 2(*a*), curve *2*]. The continuous addition of acrylic acid to the reaction results in a drift of the copolymer composition throughout the copolymerization [Figure 2(*a*), curves *3–5* and Figure 2(*b*), curves *6* and *7*]. The slower the addition rate, the more drastic change in the copolymer composition [see Figure 2(*a*), curves *3–5*]. When loading acrylic acid after the start of polymerization of styrene, the most pronounced change in the copolymer composition is observed [see Figure *2*(*b*), curves *6* and *7*].

The change in the average composition of the copolymer during polymerization may involve the formation of a composition heterogeneous copolymer in conventional radical copolymerization and a composition homogeneous copolymer in RAFT copolymerization.[15]

To confirm the RAFT mechanism, we determined the average molar weight and dispersity (*Đ*) of the copolymers by size exclusion chromatography (SEC).[§] The resulting copolymers are characterized

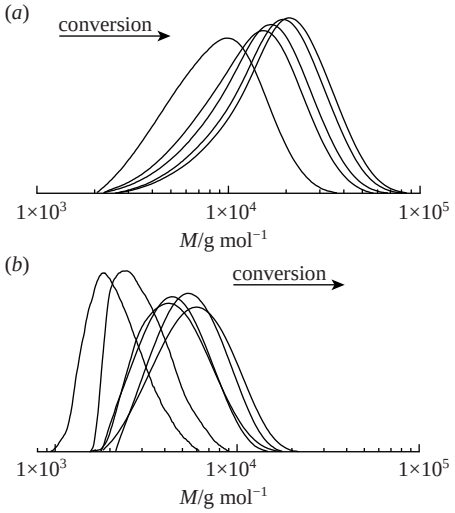


Figure 3 The SEC curves normalized by the unit area for the copolymers formed in accordance with (*a*) entry 2 in Table 1 and (*b*) entry 5 in Table 1 at various monomer conversions during RAFT copolymerization of styrene and acrylic acid.

containing the calculated amounts of AIBN (1×10^{-3} mol dm^{-3}) and BTC (6×10^{-3} mol dm^{-3}) in 1,4-dioxane was loaded into the flask, and styrene was added. Acrylic acid was dosed using a BYZ-810 syringe pump. The flask was purged with argon (99.99%) for 15 min, closed and immersed in a bath heated to 80 °C. At the specified time, samples were taken for analysis. The monomer conversion was determined gravimetrically as the weight ratio of polymer and monomers already introduced into the reaction.

‡ FTIR spectroscopy in the ATR mode (diamond crystal) was performed on a PerkinElmer Spectrum Two FT-IR spectrometer in the range 4000–600 cm^{-1}. The copolymer composition was calculated from the calibration curves as the dependence of the intensity ratio A_{1702}/A_{696}, assigned to the absorbance of acrylic acid and styrene, respectively, on the acrylic acid/styrene molar ratio.

§ Measurements were carried out in *N*,*N*-dimethylformamide containing LiBr (0.1 wt%) at 50 °C using a PolymerLabs GPC-120 chromatograph equipped with a refractive index detector and two PLgel 5 μm MIXED B columns for a molecular weight 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.

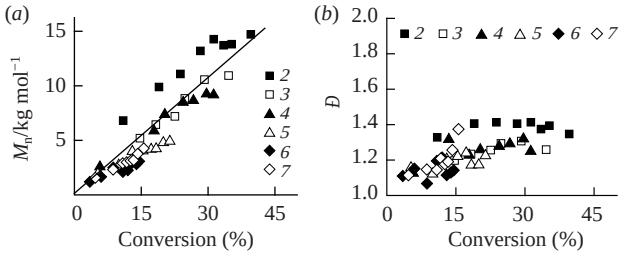


Figure 4 Dependences of (*a*) the number average molar weight M_n and (*b*) dispersity *Đ* on the monomer conversion for the copolymers formed during the RAFT copolymerization of styrene and acrylic acid with various methods of loading acrylic acid into the reaction. The symbol number corresponds to the entry in Table 1.

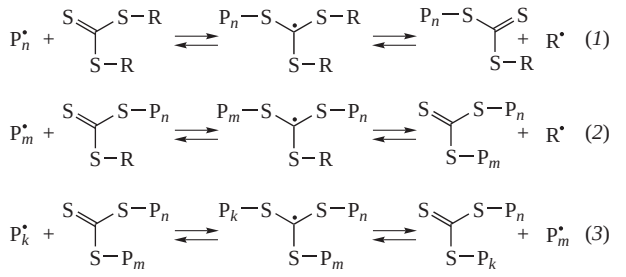


Figure 5 Illustration of the RAFT mechanism mediated by symmetrical trithiocarbonates.[15]

by unimodal molecular weight distribution (Figure 3). The SEC traces shift towards higher molecular weight with the progress of monomer conversion irrespective of the way of loading of acrylic acid into the reaction. The number average molar weight (M_n) of the copolymers increases linearly with the increase in the monomer conversion [Figure 4(*a*)], while the dispersity *Đ* in all the studied systems remains relatively low [Figure 4(*b*)]. This behavior is consistent with the RAFT mechanism. So, it can be concluded that copolymers of homogeneous composition are formed.

In the presence of symmetrical trithiocarbonates, styrene–acrylic acid copolymer macromolecules grow on two sides of the trithiocarbonate group,[12] as shown schematically in Figure 5. Thus, a change in the average copolymer composition during polymerization results in a continuous variation of the copolymer composition (or monomer sequence) of the macromolecule at both ends of its chain. So, if batch copolymerization provides the formation of a random copolymer, and continuous copolymerization leads to the formation of a gradient copolymer, then semi-continuous copolymerization gives rise to the formation of a block gradient copolymer.

In summary, it can be concluded that the method and rate of loading of acrylic acid during copolymerization with styrene make it easy to synthesize copolymers of the desired microstructure.

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