PERGAMON

European Polymer Journal 35 (1999) 1043–1046

EUROPEAN POLYMER JOURNAL

Potential bootstrap effect and phase separation of reaction solutions

Yu.D. Semchikov *, L.A. Smirnova, N.A. Kopylova, S.D. Zaitsev

Nizhny Novgorod Lobachesky State University, 23, Gagarin Avenue, 603600 Nizhny Novgorod, Russia

Received 9 March 1998; accepted 10 July 1998

Abstract

The phase separation in monomer–copolymer solutions was studied for styrene–acrylonitrile, styrene–butyl methacrylate and styrene–methyl methacrylate systems in order to find conditions to stimulate a bootstrap effect in radical copolymerization. There was phase separation at $T_{\text{sep}} < T_{\text{cop}}$ and a bootstrap effect for the styrene–acrylonitrile and styrene–butyl methacrylate system, but no effects for the styrene–methyl methacrylate system. Both the data on the phase separation and the excess free energy of the monomer mixing (ΔG^{ex}) are needed to explain the dependence of the bootstrap effect on the temperature of the styrene–butyl methacrylate copolymerization. Temperature had a large influence on the copolymer inhomogeneity in the copolymerization of styrene with butyl methacrylate in this study. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

It is known that the copolymer composition, distribution, and monomer reactivity ratios of binary copolymerization in bulk may be considerably influenced by the preferential solvation of growing chains of monomers [1, 2]. The kinetic and microstructure effects in copolymerization attributed to preferential solvation were named bootstrap effects and a copolymerization model taking these effects into consideration was named a bootstrap model [3]. It is very significant for predicting the conditions that lead to the bootstrap model realization in copolymerization. In our investigation we observed that a positive excess free energy of the mixing of two monomers $\Delta G^{\text{ex}} > 0$ is accompanied by a dynamic bootstrap effect in the bulk copolymerization of a number of systems [4]. In order to better understand what stimulates the appearance of the bootstrap effect in bulk copolymerization, we have studied the phase separation in reaction solutions, i.e. comonomer–copolymer solutions, of styrene (ST)–methyl methacrylate (MMA), ST–acrylonitrile (AN) and ST–butyl methacrylate (BMA) systems. Some experiments concerning the distribution of ST–BMA copolymer were also carried out to verify the bootstrap effect in this system.

2. Experimental

2.1. Materials

The monomers were dried and fractionated under atmospheric pressure (MMA, AN) and under vacuum (ST, BMA). The purities were checked by using gas–liquid chromatography, the purity being found to be more then 99.7%. An initiator, 2,2′–azobis (isobutyronitrile) (AIBN) was purified by recrystallization from diethyl ether and dicyclohexylperoxydicarbonate (DCC) by precipitation from an acetone solution with a mixture of methanol and water (1:2 by volume). The

---

* Corresponding author. Fax: 8 312 658 592; E-mail: chem@nnucnit.unn.ac.ru

PII: S0014-3057(98)00191-8

solvents were dried and purified by standard procedures.

2.2. Copolymerization and fractionation

The bulk ST–BMA copolymerization was carried out at 303 and 343 K up to 5 and 70 wt% conversion. The copolymerization of ST and MMA was carried out in bulk and in the presence of nonsolvents (octane, methanol). Prior to the polymerization, the monomer solutions were degassed. The process was performed in evacuated ampoules. ST–BMA copolymers were fractionated by stepwise precipitation in a methyl ethyl ketone–methanol system. The analysis of ST–BMA and ST–MMA copolymer was made by IR-spectroscopy with a "Specord-75-IR". The molecular weights were determined by viscometry and gel-permeation chromatography methods.

2.3. Determination of excess Gibbs free energy ΔG^{ex}

The excess Gibbs free energy of the monomer mixture, ΔG^{ex}, was calculated from the data on liquid–vapour equilibrium [4]. The estimation error of the values of ΔG^{ex} was less than 4%.

2.4. Determination of critical solution temperature

To determine the phase separation temperature, given amounts of the copolymer and monomers were placed into tubes, sealed and shaken until they formed a homogeneous system. Usually, 4–5 wt% solutions were prepared that corresponded to low-conversion copolymerizations. The sealed tubes were slowly cooled to determine the phase separation temperature as visual cloud points. The average value of the critical temperature was usually found by a cooling–heating cycle.

3. Copolymerization

The general bootstrap effect we have found in the homogeneous bulk copolymerization is dynamic because the preferential solvation coefficient depends on the molecular weight (M_W) of the copolymer, and, as a result, the copolymer composition depended on its M_W. According to this phenomenon, there are two main kinetic effects of the bootstrap model on the bulk copolymerization—the dependence of the copolymer composition and reactivity ratios on the initiator or chain transfer agent concentrations and the inhomogeneity in the composition of low-conversion copolymers. In the last case, we mean a larger inhomogeneity than that predicted by Stockmayer [5]. Both of the above effects were observed in ST–AN copolymerization but were not been in ST–MMA copolymerization [1]. The ST–BMA system is of great interest [6] because the dependence of the copolymer composition on its M_W takes place at 303 K and it does not occur at 343 K. For this system, there is no data concerning the copolymer inhomogeneity. It was necessary, first of all, to obtain this data to confirm the dependence of the bootstrap effects on temperature in this copolymerization.

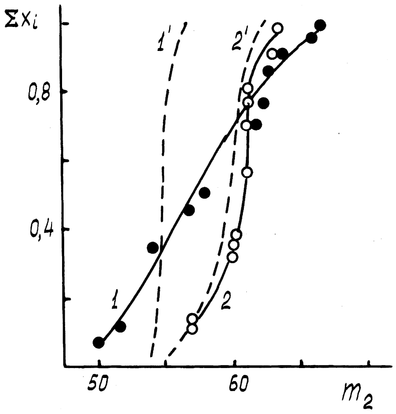

Fig. 1. Integral composition distribution curves for low-conversion ST (1)–BMA (2) copolymer obtained in bulk: 7% conversion, $M_2 = 0.7$. 1—$T = 303$ K, [DCC] $= 5 \times 10^{-3}$ M; 2—$T = 343$ K, [AIBN] $= 5 \times 10^{-3}$ M; 1′,2′—calculated according to Stockmayer [5].

As Fig. 1 shows, the inhomogeneity in composition of copoly (ST–BMA) formed at 343 K is close to the instantenous inhomogeneity calculated according to Stockmayer [5]. But the distribution in composition of

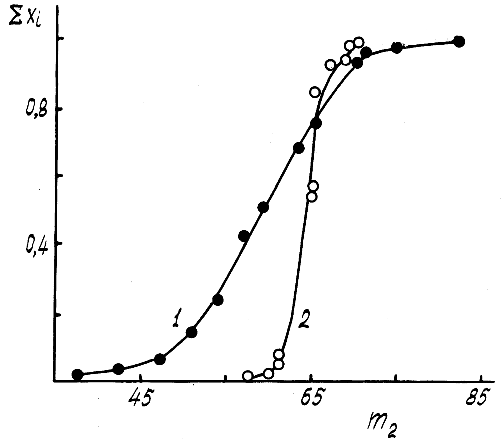

Fig. 2. Integral composition distribution curves for high-conversion ST (1)–BMA (2) copolymer obtained in bulk: 70% conversion, $M_2 = 0.7$. 1—$T = 303$ K, [DCC] $= 5 \times 10^{-3}$ M; 2—$T = 343$ K, [AIBN] $= 5 \times 10^{-3}$ M.

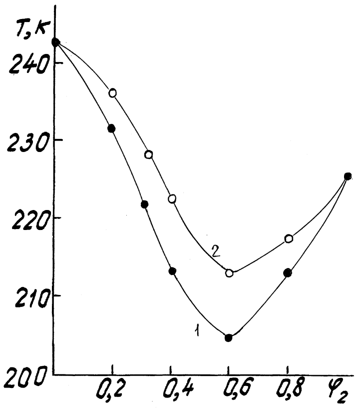

Fig. 3. The monomer freezing temperatures against the composition of ST (1)–MMA (2) monomer mixtures: 1–5wt% solutions of 32 mol% ST–68 mol% MMA copolymers, $M_\mathrm{W} = 63.3 \times 10^4$; 2—monomer mixture; φ_2—volume fraction of MMA.

the copolymer is significantly wider if bulk copolymerization proceeds at 303 K. These results confirm the bootstrap model of ST–BMA copolymerization only at 303 K. Fig. 2 shows that a large difference in the inhomogeneity of the copolymers obtained at 303 K and at 343 K is observed in high-conversion ST–BMA copolymerization also. This result is important since the conversion limit of the bootstrap model in bulk copolymerization is not yet known.

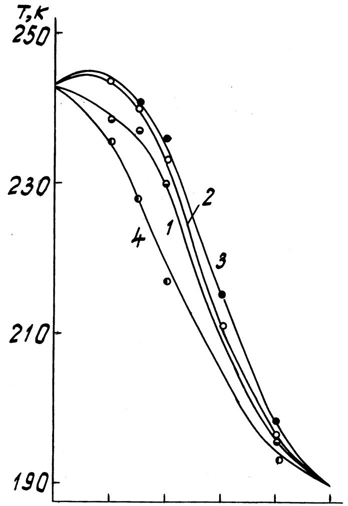

Fig. 4. Phase separation temperatures against composition of 5 wt% solutions of 60 mol% ST–40 mol% AN copolymers in ST (1)–AN (2) monomer mixtures. Copolymer M_W: 1—17×10^3, 2—1.076×10^6, 3—2.84×10^6, 4—monomer mixture; φ_2—volume fraction of AN.

4. Phase separation

Phase separation temperatures were determined for four slightly different samples. As shown in Fig. 3–5, there is no phase separation in the classical ST–MMA–copoly (ST–MMA) system until the correct freezing temperature is reached, but the upper critical solution temperatures are registrated for anomalous ST–AN–copoly (ST–AN) and ST–BMA–copoly (ST–BMA) systems. According to the Flory–Huggins theory, Θ-temperature is close to the upper critical solution temperature. Thus, one of key requirements for the bootstrap model to work may be a relative approach of the copolymerization conditions to the Θ-conditions, meaning conditions that define the thermodynamic quality of the monomer mixture as a solvent for the copolymer. It is known that the preferential solvation increases if the ternary system (solvent 1–solvent 2–polymer) approaches to the Θ-conditions [7].

One may believe that the decrease of temperature in ST–BMA bulk copolymerization stimulates the appearance of bootstrap effects because of a reaction solution approaching the Θ-conditions. This is true, but there is another aspect of the problem as well. It is seen from Figs. 5 and 6 that the upper critical solution temperatures are higher for the ST–BMA system. This means that at 343 K, the ST–BMA reaction system is closer to the Θ-temperature than ST–AN. Nevertheless, there is the bootstrap effect in ST–AN copolymerization at this temperature and no effects in ST–BMA copolymerization (see Figs. 1 and 2 and Refs. [1, 6]). In order to explain in behavior of these systems, we plotted our ΔG^{ex} data [4] against temperature. Fig. 6 shows that $\Delta G^{\mathrm{ex}} < 0$ at 343 K for the ST–

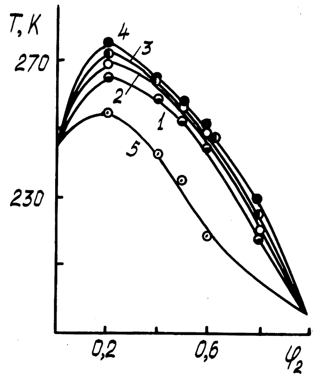

Fig. 5. Phase separation temperatures against composition of 5 wt% solutions of ST (1)–BMA (2) copolymers in ST–BMA monomer mixtures. 1,3—60 mol% ST–40 mol% BMA copolymer; 1—$M_\mathrm{W} = 0.22 \times 10^6$, 3—$M_\mathrm{W} = 1.9 \times 10^6$; 2,4—80 - mol% ST–20 mol% BMA copolymer; 2—$M_\mathrm{W} = 1.6 \times 10^5$, 4—$M_\mathrm{W} = 1.7 \times 10^6$; 5—monomer mixtures; φ_2—volume fraction of BMA.

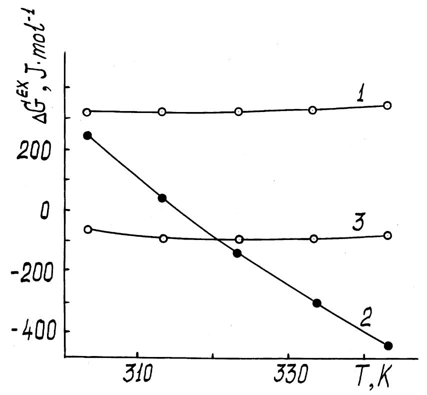

Fig. 6. Plots of excess Gibbs free energy of monomer mixture (1:1 by mole) ΔG^{ex} against temperature for ST–AN (1), ST–BMA (2), and ST–MMA (3) systems.

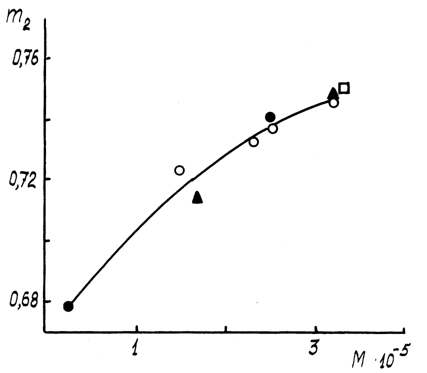

Fig. 7. Dependence of copolymer composition on M_{W} in homogeneous ST (1)–MMA (2) copolymerization in nonsolvents; 333 K, [AIBN] = 5×10^{-3} M, $M_2 = 0.8$; 33 vol% methanol, [$C_{12}H_{25}SH$] = 2.5×10^{-3}, 5×10^{-3} M (●); 60, 50, 33 and 20 vol% methanol (○); 60 and 33 vol% octane (▲); bulk copolymerization (□).

BMA monomer mixture and, according to Ref. [4], the dynamic bootstrap effect does not take place under these conditions. It seems that two factors are important for the bootstrap model realization in bulk copolymerization. The first is the sign of the excess free energy of monomer mixing $\Delta G^{\mathrm{ex}} > 0$ and the second is a relatively poor monomer mixture as a solvent for the copolymer. The latter takes place under copolymerization conditions which are not very far from the phase separation conditions of the reaction system. For a dynamic bootstrap effect, the decrease of the second virial coefficient A_2 of the monomer–copolymer solution with an increase in the copolymer M_{W} is important as well [1].

There is another way of making the monomer mixture poorer as a solvent for the copolymer. It is necessary to add a quantity of a nonsolvent to the solvent. According to this idea, the copolymerization of a 20 mol% ST–80 mol% MMA mixture in methanol and octane as nonsolvents was studied. The copolymer M_{W} was controlled by the nonsolvents as very weak chain-transfer agents. To obtain a very low M_{W} copolymer, decyl mercaptan was also used as a strong chain-transfer agent. Both nonsolvents lead to heterogeneous ST–MMA copolymerization if their content is more than 54 vol% in the monomer mixture. We used a lesser amount of the nonsolvents in order to have homogeneous copolymerization. The results are summarized in Fig. 7. It is seen that the nonsolvents cause the copolymer composition dependence on M_{W}. As mentioned above, the bulk ST–MMA copolymerization is classic.

Acknowledgements

The research discussed in this paper has been made possible by the Russian Foundation of Fundamental Researches (project 96-03-32744a).

References

[1] Semchikov YuD, Smirnova LA, Knyazeva TYe, Bulgakova SA, Sherstyanykh VI. Eur Polym J 1990;26(8):883.
[2] Semchikov YuD. Makromol Chem Macromol Symp 1996;111:317.
[3] Harwood HJ. Makromol Chem Macromol Symp 1987;10/11:331.
[4] Egorochkin GA, Semchikov YuD, Smirnova LA, Karyakin NV, Kut'in AM. Eur Polym J 1992;28(6):681.
[5] Stockmayer WH. J Chem Phys 1945;B13(6):199.
[6] Semchikov YuD, Smirnova LA, Kopylova NA, Izvolenskii VV. Eur Polym J 1996;32(10):1213.
[7] Katime I, Garro P, Telion JM. Eur Polym J 1975;11:881.