The ratio of refractive index and molecular weight of copolymers of n-butyl acrylate and styrene obtained by the method of RAFT-radical polymerization

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Abstract. The kinetic and molecular weight characteristics of the copolymers of n-butyl acrylate and styrene (95: 5 wt.%) obtained by the method of radical polymerization with reversible chain transfer were studied. The dependence of the refractive index on the molecular weight of the copolymers of n-butyl acrylate and styrene is shown.

1. Introduction
A promising method for controlling the processes of macromolecule formation is radical polymerization proceeding by the mechanism reversible addition fragmentation chain transfer (RAFT). The main difference between RAFT polymerization and conventional radical polymerization is the suppression of the quadratic death of macroradicals due to their reversible interaction with special substances – RAFT agents, compounds with di- or tri- tiocarbonate groups [1-10]. As a result of the addition of a macroradical in the double bond C=S, radical intermediates are formed, the fragmentation of which leads to a reactivation of the macroradicals, which further participate in the chain propagation reaction. The use of these processes makes it possible to effectively control copolymerization to obtain compositionally uniform copolymers with given molecular weights and a narrow molecular weight distribution from monomers that differ in their activity [10–16], which is difficult to achieve with traditional synthetic methods.

Light refractive index (nD) is one of the most important characteristics of any transparent material, including polymeric, used for the manufacture of various optical elements. At constant temperature and pressure, the value of the refractive index depends on the composition and chemical nature of the polymer.

The purpose of this work is to establish the ratio of refractive index and molecular weight of butyl acrylate and styrene copolymers obtained by radical RAFT copolymerization. These elastomers of n-butyl acrylate and styrene can be used as promising high-impact modifying additives in the production of polymethyl methacrylate glasses [17]. In order to maintain the optical transparency of plexiglass, it is necessary that the elastomeric additive be compositionally uniform and have a refractive index equal to that of polymethyl methacrylate (PMMA) [18].

2. Materials and Methods
As the main monomer used n-butyl acrylate (BA) (Aldrich ≥ 99%). Styrene (ST) was used as a comonomer that regulates the refractive index of an elastomer, which was purified from hydroquinone with a 10% aqueous NaOH solution, washed with distilled water until neutral, dried over calcined CaCl₂, distilled and thawed in vacuum (<0.01 mm. hg).
Dibenzyl trithiocarbonate (BTC) synthesized by a known method [19, 20] was used as an agent for reversible transfer of the radical polymerization chain. 2,2'-azo-bis-isobutyronitrile (AIBN), which was purified from impurities by recrystallization from ethanol, was used as an initiator.

The radical copolymerization of BA and ST was carried out in a toluene solution in sealed glass ampoules. Oxygen dissolved in the mixture was removed in a vacuum unit with repeated repetition of the freeze-thaw cycle in liquid nitrogen to a residual pressure of 0.01 mm hg. The calorimetric method in isothermal mode \(T = 80^\circ C\) on a Calve DAK-1-1 microcalorimeter recorded the heat release rate, from where the reduced copolymerization rate was determined from the known polymerization heats of BA and ST (83.3 and 73.8 kJ/mol, respectively [21]) and built kinetic curves. Companion ampoules in which \(\sim 5\) g of copolymers were synthesized were placed in an air thermostat \(T=80^\circ C\), and polymerization was carried out to the maximum conversion.

The molecular mass characteristics of the synthesized copolymers were determined by size-exclusion chromatography (SEC) on a Waters Alliance GPCV 2000 chromatograph equipped with a differential refractometer \((RI)\) and a multi-angle laser light scattering detector \((MALLS)\).

The refractive index \((n_D)\) of the copolymers was determined using an IRF-22 laboratory refractometer (wavelength 589.3 nm) at \(T = 20^\circ C\).

3. Results and discussion

We synthesized copolymers of BA and ST (95:5 wt.%) in a toluene solution by radical polymerization in reversible addition fragmentation chain transfer (RAFT). By varying the initial concentration of the RAFT agent calculated from the law of “living” chains, the molecular weight of the copolymers was varied within the range of \(MM = 5000-200000\). The conditions for the synthesis of copolymers are presented in Table 1.

| \(\text{No}\) | \(M_{\text{calc}}, \text{g/mol}\) | [BA], mol/l | [ST], mol/l | [BTC], mol/l |
|---|---|---|---|---|
| 1 | 5000 | | | 0.078 |
| 2 | 10000 | | | 0.039 |
| 3 | 50000 | 3.27 | 0.21 | 0.008 |
| 4 | 100000 | | | 0.004 |
| 5 | 200000 | | | 0.002 |

The kinetic curves (Figure 1) show that the initial polymerization rate in all cases is almost the same value, which is due to the same initial concentration of the initiator. However, an increase in the reduced polymerization rate is observed, the intensity of which depends on the initial concentration of the RAFT agent. The lower the concentration of BTC, the stronger the growth of \(W/M\). The maximum values of the reduced polymerization rate also depend on the concentration of BTC, which is due to the partial death of growth radicals by reaction with the intermediate [22–26], which leads to a slowdown in the polymerization reaction. On the whole, an increase in the polymerization rate is not associated with the effect of the auto-acceleration of polymerization at a high degree of conversion, due to the diffusion-controlled reaction of quadratic chain termination, since the reaction proceeds in a 50% toluene solution, but is associated with a change in the current ratio of BA and ST concentration since their copolymerization constants \((r_1 = 0.2, r_2 = 0.8)\) [21] contribute to the formation of an alternating copolymer with the predominant incorporation of styrene units into the composition of the copolymer.
Therefore, when styrene is deficient, its conversion exceeds the conversion of n-butyl acrylate and the monomer ratio increases in favor of n-butyl acrylate, whose homopolymerization constant is more than an order of magnitude higher than styrene homopolymerization constant ($k_{pBA} = 5800 \, l/mol \, s$, $k_{pST} = 300 \, l/mol \, s$) [21].

The use of RAFT polymerization makes it possible to obtain compositionally uniform copolymers as compared to classical radical polymerization, in which compositionally nonuniform copolymers are formed due to the difference in copolymerization constants [21]. In compositionally nonuniform copolymers, some of the polymer chains that make up the polymer product can have different refractive indices that affect the optical properties of the polymer product [27, 28].

SEC analysis of the samples showed that the molecular weight distribution curves of BA and ST copolymers are unimodal in nature and have a narrow distribution. It can be seen (Figure 2) that the chromatographic curves shift toward higher molecular weights during the transition from experiment 1 to experiment 5 (Table 1). It is seen (see Table 2) that the absolute molecular masses of the copolymers in experiments 1 and 2 coincide with the set values and the polydispersity $M_w/M_n$ is 1.2, which indicates the implementation of “living” chains mode under the given conditions of copolymerization. With a decrease in the concentration of the RAFT agent (BTC), the polydispersity parameter increases, which is due to the occurrence of the mixed “living” mode and conventional radical polymerization. This is also confirmed by the fact that the experimental molecular weights of the copolymers in experiments 3-5 strongly differ from the calculated molecular weights. The main reason is the high concentration of AIBN initiator, which did not change from experiment to experiment and was chosen for polymerization under the conditions of experiment 1 at the highest concentration of BTC.

**Figure 1.** Kinetic curves of the radical RAFT copolymerization of BA and ST in the coordinates “reduced polymerization rate $W/[M]$ - time $t$” (a), “reduced polymerization rate $W/[M]$ - double bond conversion $C$” (b). Conditions according to table 1.
Figure 2. SEC curves of BA and ST copolymers synthesized under the conditions of experiments in Table 1. detected by a refractometric detector (RI) (a) and a multi-angle laser light scattering detector (MALLS) (b).

Table 2. - Molecular mass characteristics of BA and ST copolymers synthesized under the experimental conditions in table 1.

| №  | $M_n$  | $M_w$  | PDI | $M_n$  | $M_w$  | PDI  |
|----|--------|--------|------|--------|--------|------|
| 1  | 3200   | 5400   | 1.7  | 5400   | 6500   | 1.2  |
| 2  | 4100   | 9200   | 2.2  | 9400   | 10900  | 1.2  |
| 3  | 5900   | 21200  | 3.6  | 16700  | 24700  | 1.5  |
| 4  | 6000   | 24700  | 4.1  | 19400  | 30400  | 1.6  |
| 5  | 5800   | 29600  | 5.1  | 22300  | 36800  | 1.7  |

IR spectra (Figure 3) of BA and ST copolymers were recorded in the regime of impaired total internal reflection. The IR spectra show characteristic absorption bands of the functional groups of poly(n-butyl acrylate) in the region of 1730 cm$^{-1}$, corresponding to stretching vibrations of the C=O bond and polystyrene in the region of 700 cm$^{-1}$, corresponding to vibrations of C-H bonds. IR spectra with different molecular weights are of a similar nature, which indicates the inclusion in the composition of the copolymers of units of both monomers and a qualitatively identical composition of BA and ST copolymers of different molecular weights.

Figure 3. IR spectra of BA and ST copolymers synthesized under the experimental conditions in Table 1.

Figure 4. The dependence of the refractive index $n_D$ on the molecular weight $M_n$ of the BA and ST copolymer.
For BA and ST copolymers, the refractive index \((n_D)\) was determined on an Abbe refractometer. The refractive indices of BA and ST copolymers are \(n_D = 1.481 \div 1.472\). From Figure 4 shows that the refractive index decreases with an increase in the molecular weight \((M_n)\) of the copolymer and, accordingly, with a decrease in the concentration of fragments of the RAFT agent present in the copolymer.

4. Conclusion
Using the RAFT polymerization method, compositionally uniform copolymers of n-butyl acrylate and styrene with different molecular weights were synthesized as promising impact-resistant modifying additives in the production of polymethyl methacrylate glasses. A decrease in the reduced maximum rate of the “living” radical copolymerization of BA and ST with an increase in the concentration of RAFT agent was shown. It was found that with an increase in the molecular weight of the \(M_n\) copolymer, and, accordingly, an decrease in the number of dibenzyl trithiocarbonate fragments in the polymer chain, a linear decrease in the refractive index of the copolymers of n-butyl acrylate and styrene occurs.

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