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Styrene/alkylacrylate copolymers: Relationship between molecular structure and properties

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ABSTRACT

To investigate the influence of copolymer molecular structure on its properties five copolymer types of styrene (St) with *tert*-butylactylate (tBA) and St with methylacrylate (MA) were synthesized. Gradient, block-random and diblock-copolymers were obtained via NMP polymerization using SG1 and TEMPO as reversible inhibitors. Random homogeneous and heterogeneous copolymers were synthesized using conventional radical polymerization. Peculiarities of phase separation in these copolymers were investigated by AFM and DSC. Gradient and random heterogeneous St/MA (F_{St} = 30 mol%) copolymers have heterophase structure with similar main phase ($F_{St} \approx 45$ mol%) that specifies T_g and mechanical properties of entire copolymer. Thus gradient and random heterogeneous have approximately the same tensile strength (25 MPa) and modulus (0.5 GPa), whereas random uniform copolymer behaves like typical rubber (modulus 35 MPa and strain about 600%) since it has $T_g = 18$ °C. St/tBA copolymers have homogeneous structure with the same $T_g = 59$ °C independently on chain structure.

1. Introduction

The creation of new polymeric materials with the required combination of properties is of great practical importance.

Because of influence of copolymer structure on its properties the estimation of relationship between composition, chain distribution and bulk properties is of great scientific interest for this purpose. For example, styrene/acrylates copolymers obtained in emulsion polymerization were studied in details [1–6].

In recent years, the methods of controlled copolymerization have gained wide acceptance for creation new polymer structures. With the use of the known monomers, these methods make it possible to perform the controlled synthesis of copolymers with the desired molecular mass, structure, and chain architecture. An example of such compounds is gradient copolymers, which are a comparatively new class of copolymers, in which the composition of macromolecules varies gradually from head to tail. This structure of gradient copolymers determines the features that distinguish them from other types of copolymers. For example, other conditions being equal, gradient copolymers have lower glass transition temperatures, higher transparency, and better strength than their statistical analogs [7,8]. There are several works, related to investigation of various properties of gradient copolymers and their mixtures with homopolymers [9–15].

This study concerns the synthesis of five copolymer types of St with tBA and St with MA including gradient and block copolymers and investigation of structure and various properties of gradient copolymers compared with other types of copolymers.

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2. Experimental

2.1. Materials and methods

Styrene, tBA and MA ("Aldrich") were purified conventionally. Immediately before use, the monomers were recondenced in vacuum. AIBN was recrystallized from ethanol, dried in vacuum to a constant weight, and kept at −18 °C. TEMPO ("Sigma") and cumene hydroperoxide (CHP) ("Sigma") were used as received.

Polymerization was performed in glass ampoules, the reaction mixture was degassed to a residual pressure of 10^{-2} mm Hg, and the ampoule was sealed. Polymers were lyophilized from benzene solutions.

^{1}H NMR spectra were measured on a Bruker AC200P instrument operating at a frequency of 200.13 MHz. Chemical shifts in ^{1}H NMR spectra (ppm) were presented on the δ scale relative to tetramethylsilane.

The molecular mass characteristics of the polymers were determined by GPC at 35 °C relative to pSt standards on a Waters liquid chromatograph equipped with refractometric and UV detectors, three columns packed with ultrastyragel with pore sizes of 10^3 Å and 10^5 Å, and one linear column. Chromatograms were processed on a Data Module 730 integrator.

Thin films surface investigation was performed by AFM on FemtoScan and Nanoscope IIIa microscopes using fpN10S kantilevers (F.V. Lukin FGUP NIIFP) in semicontact regime.

Differential scanning calorimetry (DSC) was performed on Netzsch DSC 204 Phoenix at a heating rate of 10 °C min^{-1} and an Ar purge rate of 50 ml min^{-1}.

Mechanical properties were estimated on Tinius Olsen H5KS at 50% min^{-1} deformation rate.

Optical density were measured on Ultrospec 500/1100Pro at 600 nm.

2.2. Polymer synthesis

2.2.1. Synthesis of St/tBA copolymers (Run B1–B5)

2.2.1.1. Synthesis of random homogeneous copolymers.

(A) Synthesis of random homogeneous copolymer with $F_{St} = 30\%$ (here and after mol%) (Run B1).

AIBN (0.067 g) was dissolved in the mixture of 1.2 ml St and 8.8 ml tBA. Polymerization was carried out at 60 °C for 30 min.

(B) Synthesis of random homogeneous copolymer with $F_{St} = 43\%$ (Run B1*)

AIBN (0.0017 g) and TEMPO (0.0019 g) using dilution method were added to the mixture of 0.25 ml St and 0.75 ml tBA. Polymerization was carried out at 120 °C for 40 min.

2.2.1.2. Synthesis of gradient copolymer (Run B2). AIBN (0.0033 g), TEMPO (0.0038 g) and CHP (0.0018 g) using dilution method were added to the mixture of 0.5 ml St and 1.5 ml tBA. Polymerization was carried out at 120 °C for 24 h.

2.2.1.3. Synthesis of random heterogeneous copolymer (Run B3). AIBN (0.074 g) was added to the solution of 0.5 ml St and 1.5 ml tBA in 8 ml benzene. Polymerization was carried out at 60 °C for 24 h.

2.2.1.4. Synthesis of St/tBA block-copolymer (Run B4). Macroinitiator PS-SG1 (0.8 g) ($M_n = 13700$ PDI = 1.4) [17] containing 9 mol% of free SG1 was dissolved in 5 ml of tBA. Polymerization was carried out at 120 °C for 1.5 h.

2.2.1.5. Synthesis of p(St-tBA)-poly-tBA copolymer (Run B5). Random-gradient St/tBA copolymer was synthesized in 2 steps. At first adducts of random St/tBA copolymer with TEMPO (p(St-tBA)-TEMPO) were obtained and used as initiator at the second step.

Step 1. AIBN (0.0016 g) and TEMPO (0.0019 g) using dilution method were added to the mixture of 0.25 ml St and 0.75 ml tBA. Polymerization was carried out at 120 °C for 14 h.

Step 2. p(St-tBA)-TEMPO adducts (1.5 g) and CHP (0.0045 g) using dilution method were added to the mixture of 0.5 ml St and 10 ml tBA. Polymerization was carried out at 120 °C for 10 h.

2.2.2. Synthesis of St/MA copolymers (Run M1–M4)

St/MA copolymers were synthesized in the same way as St/tBA ones. The differences in conditions are listed in Table 1.

3. Results and discussion

3.1. Peculiarities of gradient and random heterogeneous copolymers synthesis

Random heterogeneous copolymers were obtained via free radical polymerization that includes the following main steps:

1. Initiation: $I \to 2R^{\bullet}$
2. Propagation: $R^{\bullet} + M \to P_n^{\bullet}$
3. Termination: $P_n^{\bullet} + P_m^{\bullet} \to P_{n+m}$

Gradient copolymers are obtained in pseudo-living radical polymerization that proceeds as follows:

1. Initiation: $I \to 2R^{\cdot}$
2. Propagation: $R^{\cdot} + M \to P_n^{\cdot}$
3. Inhibition: $P_n^{\cdot} + T^{\cdot} \to P_n - \mathrm{T}$
4. Reinitiation: $P_n - T \to P_n^{\cdot} + T^{\cdot}$
5. Repeat steps 2–5

where I – initiator (AIBN); $R^{\cdot}$ – primary radical; $P_n^{\cdot}$ – propagating radical; M – monomer; $T^{\cdot}$ – nitroxide TEMPO or SG1.

Thus propagating chains in pseudo-living process are able to grow within the whole process whereas in free radical polymerization they undergo irreversible termination in every moment. In case of copolymerization it means that the numbers of macromolecules with different composition are obtained in free radical polymerization. As