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Nitroxide mediated styrene radical polymerization using a fluorescence marked mediator

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ABSTRACT

Polystyrenes containing fluorescence end-groups were prepared by nitroxide-mediated radical polymerization. Combined molar mass regulator contained besides alkoxyamine part the structure of fluorescence mark. Stable nitroxyl radical represented 2,2,6,6-tetramethylpiperidine-Noxyl and covalently bonded fluorescence mark was benzothioxanthene. A fluorescence method as well as UV absorption was employed for measuring the concentration of nitroxyl-terminated chains in polystyrene samples. Theoretical molar masses of polystyrenes were calculated from these concentrations on the assumption that all polystyrene chains are terminated by alkoxyamine dormant end-functionality bearing fluorescence probe. Comparisons of these data with the molar masses from GPC gave us the range of the marked active polymer chain ends. Fractions of active polymer chain ends depended on the conversion. With increased conversion the fraction of polystyrene chains terminated by alkoxyamine was decreased. From this follows that the "livingness" of polymerization process decreased with the increasing of conversion. It should result in higher extent of termination and subsequently in the increasing of polydispersity with increased conversion. Despite this the observed polydispersity was the same for all conversion and reached the value ca. 1.3. The changing viscosity is responsible for the constant polydispersity.

1. Introduction

Over the past several years attempts to moderate the reactivity of the propagating species in radical polymerization have been multifold. Nitroxide mediated radical polymerization (NMP) offers simple method for preparation of polymers with programmable construction of macromolecules [1–4]. This method permits molar mass regulation, offers polymers with rather low molar mass distribution, allows polymer preparation with desirable choice of end groups and allows preparation of block copolymers. Contrary to the anionic polymerization it does not require precise purity of monomers and is not sensitive to the moisture.

NMP is based on the ability of nitroxide to trap growing radical under the production of an alkoxyamine dormant end-functionality. Alkoxyamine at higher temperature (90–120 °C) decomposes into nitroxide and growing radical which is able to admit a part of monomer. Polymerization can be terminated at the consumption of monomer or by decreasing of temperature. Resulted polymer contains at the chain end nitroxyl radical in the form of alkoxyamine, which is able of additional growing reaction.

Quantification of active alkoxyamine-terminated chain ends represents serious problem. Up to now used approaches as nuclear magnetic resonance analysis [5] and chain extension method [6] are problematical. NMR spectroscopy is not sufficiently precise due to the low accuracy of NMR integration to quantified dormant species especially in higher molecular mass material. Chain extension method is indirect way and provides a qualitative description of the amount of alkoxylamine-terminated polymer

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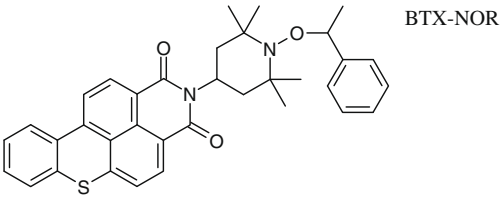
chains. The last approach – quantitative chain labeling – required substitution reaction of chain-end nitroxyl radical by another radical, which could be detectable by spectrophotometry [7]. Scaiano at al. used TEMPO as regulator of nitroxide mediated radical polymerization of styrene and from exchange reaction with high excess of coumarin-TEMPO [8] or quinoline-TEMPO [9] they calculated kinetics of exchange as well as bond energy. Nitroxide-exchange method requires conditions (123 °C, 150 min) which can change the properties of starting materials.

TEMPO derivative bearing chromophore was used by Priddy [10], Hawker [11] and Bucsiova [12]. Priddy used phenyl-azo-phenyl while Bucsiova and Hawker pyrene as chromophore. High levels of chain end incorporation were achieved only for very low molecular mass (<10,000). The content of polystyrene chains bearing TEMPO-fluorophore was decreasing with conversion increasing [12]. In another work, Hawker [13] used instead of TEMPO more efficient TIPNO (2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy skeleton). Pyrene and dimethylaminonaphthylsulfone were used as chromophores and they were attached to either the initiating fragment or the mediating nitroxide fragment. This type is better regulator for NMP than TEMPO type and it works well in the polymerization of acrylates as well. In this case the incorporation at the initiating end as well as at the nitroxide mediating end calculated on the base of extinction coefficient of fluorescence was very high 85–90% even for high conversion.

In this work we prepared polystyrenes by NMP using combined molar mass mediator containing besides alkoxyamine part the structure of fluorescence mark:



Stable nitroxyl radical represented 2,2,6,6-tetramethylpiperidine-N-oxyl and covalently bonded fluorescence mark is benzothioxanthene. Concentration of marked polystyrene chain ends in polymers was measured directly by UV-absorption or emission spectroscopy. Theoretical molar masses of polystyrenes were calculated from these concentrations on the assumption that all polystyrene chains are terminated by alkoxyamine dormant end-functionality bearing fluorescence probe. Comparisons of these data with the molar masses from GPC gave us the range of the marked active polymer chain ends – extent of "livingness". Fractionation of samples by gel permeation chromatography (GPC) and simultaneous analysis by differential refractive index and fluorescence provides a measure of the distribution of nitroxyl-terminated chain ends as a function of molecular mass. We have tried to find relationship between the extent of "livingness" and polydispersity as well as the potential of using these fluorescence marked polystyrenes with different extent of livingness as a macroinitiator. Finally it is the way how to prepare the colored polystyrenes with intense yellow fluorescence.

2. Experimental

UV–VIS absorption spectra were taken on a spectrometer UV 1650PC (Shimadzu, Japan). Emission spectra were recorded on spectrofluorophotometer RF-5301PC (Shimadzu, Japan).

Preparation of fluorescence marked regulator in the form of stable nitroxyl radical BTX-NO {2-(1-Oxo-2,2,6,6-tetramethyl-4-piperidyl)thioxantheno[2,1,9-dej]isoquinoline-1,3-dione} was described in [14] and alkoxyamine-based unimolecular initiator BTXN-OR {2-(4-(1-(1′-phenylethyl)oxy)-2,2,6,6-tetramethyl)piperidine)-thioxantheno [2,1,9dej] iso-quinoline-1,3-dione} is described in [15].

2.1. General procedure for the polymerization of styrene

Block and solution polymerization of St were carried out in sealed tubes. Monomer and regulator or macroinitiator (eventually solvent) were placed in tube, the content was bubbled with nitrogen for 10 min and sealed off. The polymerization mixture was then heated at 125 °C. Polymers were then dissolved in tetrahydrofuran and purified by precipitation in methanol (three times) and dried in vacuum. The polymers were analyzed by GPC, UV–VIS and fluorescence spectroscopy.

Molecular weight distributions of polystyrene samples were obtained by size exclusion chromatography in THF by using PSS (Mainz, Germany) column setup consisted of 8×50 mm PSS SDV 5 μm guard column and three 8×300 mm PSS SDV 5 μm columns with pore sizes 10^2, 10^3 and 10^5 Å placed in a column heater set to 40 °C. Flow rate 1 mL min^{-1} was controlled by toluene as an internal standard. Loop 100 μL and polymer concentration 3 mg mL^{-1} were used. Calibration between 374 and 2,570,000 g mol^{-1} was performed by PSS polystyrene calibration kit. PSS WinGPC®7 was used for data acquisition and evaluation. Waters system (degasser, 515 pump, column heater, DRI 410) and Rheodyne injector 7725i were applied as the hardware. In parallel, spectrofluorometric detector Shimadzu RF-10AXL (Shimadzu Corporation, Kyoto, Japan) was employed. The excitation and emission wavelengths were set to $\lambda_{ex} = 453$ nm and $\lambda_{em} = 510$ nm. The concentration calibration curve for fluorescence detection was obtained using fluorescence probe BTX-NOR in the concentration range 9.2×10^{-7} to 1.8×10^{-4} mol L^{-1}.

3. Results and discussion

The absorption spectra of fluorescence marked mediators in organic solutions as well as in polymer matrices, are characterized in the visible region by an intense absorption band within 400–525 nm region [14]. The fluorescence spectra show an intense band within 450–700 nm [15]. BTX-NOR exhibited very intense yellow fluorescence. However, for BTX-NO the fluorescence is much less intense as a result of intramolecular quenching due to the presence of radical centre of N-oxyl type. When the probes are doped in polymer films, the difference in fluorescence intensity for BTX-NO and BTX-NOR can be clearly seen by naked eye. Naturally the polystyrenes prepared under the