Polymer 58 (2015) 36–42

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Investigation on the homogeneity of PMMA gels synthesized via RAFT polymerization

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ARTICLE INFO

Article history:
Received 29 October 2014
Received in revised form
18 December 2014
Accepted 19 December 2014
Available online 27 December 2014

Keywords:
Network inhomogeneity
RAFT polymerization
Light scattering

ABSTRACT

PMMA gels synthesized by RAFT polymerization and corresponding gels made by free radical polymerization (FRP) were characterized macroscopically by determining the shear moduli and the swelling ratios, and microscopically by dynamic light scattering (DLS) with particular emphasis on inhomogeneity. The gels were prepared in the solvent γ-butyrolactone at concentrations ranging from 13 to 20 wt% (15–22.5 vol%).

The cross-linking efficiency attained in RAFT polymerizations was significantly smaller than that obtained in corresponding FRPs. This means that in RAFT polymerizations more cross-links were wasted in network imperfections. The static fraction of the total ensemble-averaged scattering intensity determined by DLS was used as a measure of inhomogeneity. This quantity decreased with rising amount of RAFT agent and when going from FRP to RAFT polymerization. However, since the effective network density decreased concurrently, the influence of the polymerization mechanism on homogeneity is just an apparent one. The RAFT gels are not more homogeneous than the FRP gels when the comparison is based on systems having the same effective network density. On the contrary, RAFT gels prepared with a high content of RAFT agent appear slightly less homogeneous than those made with a lower content of RAFT agent or via FRP, provided gels having identical moduli are compared.

1. Introduction

In recent years, controlled radical polymerization (CRP) techniques such as nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer polymerization (RAFT) have been applied increasingly for the preparation of polymer networks [1–18]. It is anticipated that such polymerizations offer the potential to prepare networks with a more homogeneous structure than that obtained by free radical polymerization (FRP). The key differences between CRP and FRP with regard to network formation are seen as follows [1,2,4,7]: When a monomer and a cross-linker (a monovinyl and a divinyl compound, respectively) are copolymerized by CRP techniques, a large number of primary chains start growing simultaneously from the beginning of the reaction. Due to frequent deactivation, chain growth occurs slowly allowing sufficient time for chain relaxation and translational diffusion. Therefore, intermolecular cross-linking is likely to take place. In a FRP a small number of active chains are formed at any time during the entire polymerization process. These chains grow extremely fast, and because of their low concentration intramolecular cross-linking (cyclization) becomes highly probable leading to the formation of microgels in the beginning of the reaction. As the reaction proceeds to higher conversion, gelation occurs by interconnecting these microgel particles to form a continuous network. This mechanism is thought to be responsible for the heterogeneity of the networks made by FRP.

The described differences between both gelation mechanisms are supported by several experimental findings. Ide and Fukuda investigated cross-linking polymerizations using NMP [1,2]. They compared the number density of cross-links at the gel point with predictions of the Flory-Stockmayer theory and found that the experimental value was only twice as high as expected. They interpreted this finding by assuming a more homogenous network structure and a lower contribution of intramolecular cyclization. Several later studies made by applying ATRP gave similar results

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http://dx.doi.org/10.1016/j.polymer.2014.12.035
0032-3861/

[3,4,6,7]. Furthermore, in contrast to FRP, Ide and Fukuda did not find any microgel formation in the early stage of the reaction in the NMP system [2]. Norisuye et al. investigated the formation of linear chains and of networks by time resolved dynamic light scattering measurements comparing RAFT polymerization and FRP. They obtained clearly differing results for both polymerization methods [13]. Zhu et al. [8] and Yu et al. [9,10,15] studied homopolymerizations of divinyl monomers using CRP techniques. Dynamic mechanical analysis of the formed networks revealed a narrower glass transition range in the case of ATRP [10] and RAFT polymerization [15]. This fact was also taken as an indication of the formation of a more homogeneous network structure in comparison to the FRP.

Other characteristic differences between CRP and FRP networks reported in the literature concern the elastic behavior. Generally, CRP networks seem to be softer, hence less densely cross-linked, when comparing systems with identical composition. Recently, Henkel and Vana reported on networks made of butyl acrylate and 1,4-butanediol diacrylate in bulk. They obtained smaller values of the Young's modulus for RAFT polymerized systems in comparison to FRP, unless the content of cross-linker was very high [12]. Similar findings were reported by Yu et al. [15] and Crescenzi et al. [11] on RAFT polymerized networks, whereas Yu et al. [10] obtained comparable values in the case of ATRP. Zhu et al. found that only about 17% of the cross-linker molecules are used for active cross-linking in an ATRP [6].

The swelling behavior shows a corresponding behavior. Since the CRP networks are usually less densely cross-linked, they exhibit higher swelling ratios than those obtained by FRP [2,11,12,16,17].

Except for a few studies [3,5,11,17], the majority of network syntheses by CRP took place in bulk or at rather high concentrations. Matyjaszewski et al. investigated the concentration dependence of monomer conversion at the gel point for ATRP. A comparison with the Flory-Stockmayer theory revealed a higher discrepancy at lower concentrations [3]. Furthermore, from a kinetic model of a cross-linking RAFT polymerization, Wang et al. also predicted that the gel point appears postponed in a diluted system if intramolecular cyclization is present [14].

In our work we employed the RAFT copolymerization of methyl methacrylate and ethylene glycol dimethacrylate at total monomer concentrations between 13 and 20 wt% in γ-butyrolactone to generate macroscopic gels, and made a comparison with the corresponding FRP. The obtained gels were characterized macroscopically by determining the shear moduli and the swelling ratios, and microscopically by dynamic light scattering with particular emphasis on inhomogeneity. The solvent γ-butyrolactone was chosen because of its low volatility, which is essential to prevent perceptible solvent evaporation during the mechanical measurements. Furthermore, it provides sufficient contrast in light scattering experiments on PMMA. We focused on the above mentioned, rather limited concentration range because the RAFT polymerization becomes extremely slow and prone to unwanted side reactions at lower concentrations, while at much higher concentrations the resulting gels become rather rigid and the evaluation of light scattering data becomes problematic. Our results reveal that a RAFT gel is not more homogeneous than an FRP gel when the comparison is based on gels having the same modulus. RAFT gels only appear to be more homogeneous because a RAFT polymerization leads to a significantly reduced cross-linking efficiency as compared to FRP.

2. Experimental

2.1. Materials

The solvent γ-butyrolactone (GBL) (Acros Organics, 99+%) and the RAFT agent 2-cyano-2-propyl 4-cyanobenzodithioate (Aldrich, 98%) were used as received. The monomers methyl methacrylate (MMA) (Aldrich, 99%, $\leq$30 ppm MEHQ) and ethylene glycol dimethacrylate (EGDMA) (Aldrich, 98%, 90–110 ppm MEHQ) were stored in a fridge and stirred with an inhibitor remover for 30 min before use to remove the stabilizer, hydroquinone monomethyl ether (MEHQ). The initiator azobisisobutyronitrile (AIBN) was recrystallized in absolute ethanol, dried at room temperature under vacuum and stored in a fridge.

2.2. Copolymerizations

2.2.1. RAFT polymerization

Gels were prepared by copolymerizing methyl methacrylate and ethylene glycol dimethacrylate in γ-butyrolactone using azobisisobutyronitrile as an initiator and 2-cyano-2-propyl 4-cyanobenzodithioate as the RAFT agent. In one series of experiments, the total monomers concentration was kept constant at 17.3 wt% (20 vol%). Three subsets were prepared with the molar ratio of RAFT agent and polymerizable vinyl groups being 1:200, 1:400, and 1:600, while the mole fraction x_{EGDMA} of EGDMA in the total monomers content varied in the range 0.02–0.06, 0.02–0.04, and 0.01–0.03, respectively. Thus, the number of cross-links per primary chain was expected to lie between 8 and 36. In a second series, the total monomers concentration was varied between 12.9 and 19.6 wt% (15 and 22.5 vol%), also with various x_{EGDMA}. This was done at a constant ratio of RAFT agent and vinyls of 1:200. The molar ratio of AIBN and vinyls was always 1:600.

To detail the procedure, we describe as an example the synthesis of a gel with 17.3 wt% monomers, $x_{\mathrm{EGDMA}} = 0.03$, and a RAFT-to-vinyls ratio of 1:200: 0.058 g (0.235 mmol) RAFT agent and 0.013 g (0.078 mmol) AIBN were dissolved in 20 mL GBL. 4.7 mL (44.3 mmol) MMA and 0.259 mL (1.37 mmol) EGDMA were added. The Schlenk flask was sealed with a rubber septum and the solution was degassed by three freeze-pump-thaw cycles. Afterwards the flask was filled with nitrogen. Using nitrogen purged syringes and filters, the reaction solution was divided into glass tubes (for rheological and swelling measurements) and NMR-tubes (for dynamic light scattering measurements), which were then screwed with plastic caps, sealed with parafilm, and kept in a preheated block in an oven at 60 °C for 72 h to ensure complete reaction.

In preliminary experiments, linear PMMA was synthesized in order to verify that the polymerization occurs in a controlled manner. The procedure was the same as described above, except that no EGDMA was added and that samples were drawn during polymerization, which were immediately analyzed with regard to conversion by NIR-spectroscopy and to molecular weight and polydispersity by GPC (Details are given in supplementary data.).

2.2.2. Free radical polymerization (FRP)

For comparison, free radical polymerizations were conducted using the same monomer concentrations and amounts of EGDMA. The procedure was the same as for the RAFT polymerizations except that no RAFT agent was added.

2.3. Rheological measurements

Elastic moduli were determined by subjecting cylindrical samples of the gels to oscillatory uniaxial compression experiments using a home-built apparatus. Such samples were obtained by breaking the glass tubes where synthesis had taken place, and cutting even front surfaces by hand. A sinusoidal deformation (typical frequency 1 Hz) was applied, and deformation and stress acting on the sample were measured by suitable inductive and piezoelectric transducers. Correlating the two signals by a gain-phase analyzer (Solartron) and applying the appropriate