

SEC/MALLS Measurement of the Branched Structure of Methyl Methacrylate + Ethylene Glycol Dimethacrylate Copolymers Synthesized by Atom Transfer Radical Polymerization

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Introduction

In the last few years, atom transfer radical polymerization (ATRP) of acrylate and methacrylate monomers in the presence of a small amount of cross-linker has been investigated in order to produce branched polymers and gels with applications in microelectronics, coatings industries or biomedicine (Wang and Zhu, 2005; Gao et al., 2007). In this context, it is being explored the production by ATRP of branched/crosslinked polymers with a lower degree of heterogeneity than that obtained by conventional free radical polymerization (FRP). This work reports an experimental study on the ATRP of methyl methacrylate (MMA) + ethylene glycol dimethacrylate (EGDMA) initiated by MBPA (methyl α -bromophenylacetate) and mediated by copper bromide (CuBr) ligated with HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetramine). The synthesized copolymers were analyzed by size exclusion chromatography (SEC) with simultaneous detection of refractive index (RI) and multi-angle laser light scattering (MALLS) signals. Important details of the molecular architecture of these materials can therefore be measured, namely absolute molecular weights and z -average radius of gyration. Different experimental runs were performed in order to investigate the influence of the operating conditions (e.g. temperature and initial molar ratios MMA/EGDMA/MBPA/CuBr/HMTETA) on the structure of the products.

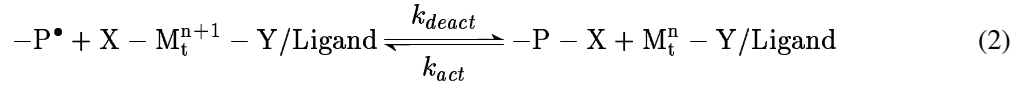
In conventional radical polymerization (FRP), the expected life time of a radical t_l is very short (of the order of 1 s) owing to the termination reaction according to Eq. (1):

$$t_l = \frac{R}{r_t} \simeq \frac{1}{2k_t R} \quad (1)$$

In this equation, R represents the concentration of radicals, r_t the rate of termination and k_t the correspondent rate coefficient. However, with ATRP the expected life time of a radical can attain several hours, since it is determined by the dynamic equilibrium between activated and deactivated states according to

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Eq. (2):



Here, $-P^{\bullet}$ represents a radical in a polymer molecule, $X - M_t^n - Y/\text{Ligand}$ a transition metal complex (e.g. $\text{Cu(I)Br}/\text{HMTETA}$), $X - M_t^{n+1} - Y/\text{Ligand}$ the correspondent oxidized metal complex (e.g. $\text{Cu(II)Br}_2/\text{HMTETA}$) and $-P - X$ a dormant radical. This intermittent exchange reduces the concentration of growing radicals and therefore minimizes the termination reactions (usually less than 5% of the total polymer chains undergoes termination in ATRP). The more usual applications of the almost “living” character of ATRP are the synthesis of low polydispersity linear polymers and of block copolymers. Nevertheless, it will be shown next that it is also useful for the controlled production of well defined hyperbranched polymers and comparatively much more homogeneous networks than those achieved by conventional radical polymerization, as the effect of intramolecular reactions is decreased.

Experimental Part

Polymerization runs were carried out using a 2.5 dm³ maximum capacity stainless steel reactor (Gonçalves et al., 2007). Anisole at 99% purity, N,N-dimethylformamide at 99.8% purity, toluene at 99.7% purity, MBPA at 97% purity, HMTETA at 97% purity, Cu(I)Br at 98% purity, MMA stabilized with 10 to 100 ppm monomethyl ether hydroquinone at 99% purity and EGDMA stabilized with 100 ppm monomethyl ether hydroquinone at 98% purity have been purchased from Sigma Aldrich and used as received. MMA, EGDMA, solvent(s), CuBr and HMTETA were premixed at 60 °C for at least 30 min in a volumetric flask. This mixture was charged to the reactor (previously purged with argon) and brought up to the desired temperature. The initiator (MBPA) was rapidly added to the system and its introduction is used to define the zero reaction time $t = 0$. Argon was bubbled in the reactor during the whole polymerization. At prescribed polymerization times, samples of polymer were withdrawn from the reactor and analyzed by SEC/RI/MALLS. A poor solubility of copper species in the polymerization system was observed when toluene was used as solvent. This difficulty was not eliminated by extending the mixing period, increasing the temperature or using a higher initial molar ratio HMTETA/ CuBr . Better results could be obtained by excluding toluene (therefore using bulk MMA) or adding DMF as a solvent (Pascual et al., 1999) even in a small amount (10%). Good solubility could also be achieved by using anisole (Xia and Matyjaszewski, 1997) + DMF as a co-solvent.

Kinetic Modeling

As described in previous works (Costa and Dias, 2007, 2005; Dias and Costa, 2007, 2006), it is possible to obtain the generating functions (GF) of molecular size distributions (MSD) of the rate equations of formation of polymer species by chemical reactions ($G_{\mathcal{R}_P}$, $G_{\mathcal{R}_S}$ and $G_{\mathcal{R}_{H_n}}$). The insertion of these GF in the population balance equations (PBE) of a non-steady state perfectly mixed continuous stirred tank reactor (CSTR) yields PBE in terms of the GF of size distributions of mole concentrations of polymer degrees of polymerization, sequences and pendant chains, $G(\mathbf{s})$, $U(\mathbf{s})$ and $G_n^H(\mathbf{s}^-, \mathbf{s}^+)$, respectively:

$$\frac{\partial G}{\partial t} = G_{\mathcal{R}_P} + \frac{G_F(t) - G}{\tau} - \mathcal{R}_v G; \quad G|_{t=0} = G_0[\mathbf{s}_0(t, \mathbf{s})] \quad (3)$$

$$\frac{\partial U}{\partial t} = G_{\mathcal{R}_S} + \frac{U_F(t) - U}{\tau} - \mathcal{R}_v U; \quad U|_{t=0} = U_0[\mathbf{s}_0(t, \mathbf{s})] \quad (4)$$

$$\frac{\partial G_n^H}{\partial t} = G_{\mathcal{R}_{H_n}} + \frac{G_{n,F}^H(t) - G_n^H}{\tau} - \mathcal{R}_v G_n^H; \quad G_n^H|_{t=0} = G_{n,0}^H [\mathbf{s}_0^-(t, \mathbf{s}^-), \mathbf{s}_0^+(t, \mathbf{s}^+)] \quad (5)$$

Eqs. (3)-(5) are non-linear first order partial differential equations solvable by the method of the characteristics. These master equations allow the prediction of the MSD, SSD (sequence size distribution) and RG (radius of gyration) distributions for general irreversible non-linear polymerizations. For the present chemical system, modeling studies were carried out considering a kinetic scheme comprising a total of 22 species and 44 different chemical reactions, as summarized in Table 1. Due to its generality, this method can be applied to different chemical systems and reactors (e.g. semi-batch), as recently shown for conventional (Gonçalves et al., 2007) and nitroxide-mediated non-linear radical copolymerizations.

Table 1: Chemical groups and kinetic scheme considered in the modeling of ATRP of MMA/EGDMA.

Chemical Groups	Chemical Reactions
Three monomers: MMA, EGDMA and pendant double bonds (PDB). Three polymer growing radicals. Three polymer dormant radicals. Initiator and radical from initiator. Complex metal/ligand and deactivator. Solvent and correspondent primary radical.	Activation/deactivation of initiator and radicals. Initiations of monomers and PDB. Propagations of monomers and PDB. Chain transfers to monomers and solvent. Combination and disproportionation.

Results and Discussion

Figure 1(a) compares experimental observations and predictions for monomer conversion in ATRP copolymerizations of MMA/EGDMA at different temperatures. A good agreement between predictions and measurements is observed using kinetic parameters available in literature for linear polymerizations (e.g. Al-Harhi et al. (2007), Zhang and Ray (2002) and references therein). Notice that the reactivity of pendant double bonds of EGDMA have a minor impact in the global monomer conversion but strongly affects the gelation phenomenon, as will be discussed below. Figure 1(b) compares experimental measurements and predictions of \overline{M}_n and \overline{M}_w in linear ATRP polymerizations of MMA at different temperatures. Good agreements are also observed at low temperatures but major deviations are identified at 90 °C possibly due to side reactions and loss of termination control which is known to occur in ATRP at high temperatures.

Figure 1(c) shows the RI chromatograms of ATRP synthesized polymethylmethacrylate (PMMA) samples at different polymerization times. The living character of this polymerization is confirmed by the observed growth of the molecular weight (MW) without a concomitant raise of polydispersity index (PDI). Figure 1(d) shows the good control of the molecular architecture achieved with ATRP for linear polymerization systems.

Predicted and observed time evolution of \overline{M}_w in linear and crosslinked polymers obtained in the ATRP copolymerization of MMA/EGDMA are compared in Figure 1(e). Here a system with a mole fraction of EGDMA of 0.5% was considered. From Figure 1(e) it is clear the influence of a small amount of crosslinker in the properties of the resulting materials, namely in comparison with the linear analogs. It is also shown the possibility of synthesize soluble hyperbranched polymers (without gelation) using living polymerization instead of conventional radical polymerization (FRP). A good agreement is also observed between predictions and measurements of \overline{M}_w in the non-linear polymerization system. Nevertheless, it should be mentioned that the most important kinetic parameter governing the crosslinking process is the

reactivity of the pendant double bonds (PDB) of EGDMA. In the present work this parameter was used to fit the experimental data and the reactivity ratio between PDB of EGDMA and MMA double bonds, $r = k_p^*/k_{p11} = 0.45$ was estimated. The decrease in the reactivity of PDB here estimated is consistent with other measurements neglecting the effect of intramolecular cyclizations in diluted systems (see for instance Gonçalves et al. (2007) and references therein) but is not in agreement with findings for bulk polymerizations stating the equal reactivity of PDB and double bonds of monovinyl monomers (Ide and Fukuda, 1997). This means that the reactivity ratio here estimated is likely an apparent value affected by the neglected influence of intramolecular cyclizations which may become appreciable already for the 50 % dilution used in our experiments. Similar findings about the importance of cyclizations have been recently reported by Matyjaszewski group in the synthesis of polyacrylate networks by ATRP (Gao et al., 2008). Complementary studies concerning reaction runs in bulk should yield a more complete assessment on the possibilities of this synthetic method to prepare well defined hyperbranched polymers and networks devoid of intramolecular loops.

Figure 1(f) shows the predicted and experimentally observed influence of the temperature on the z -average radius of gyration (\overline{R}_g) in ATRP copolymerizations of MMA/EGDMA with constant mole fraction of crosslinker ($y_{EGDMA} = 0.5\%$). Predictions were obtained with the same set of kinetic parameters used for the computation of molecular weights. The good agreement between experimental measurements and predictions confirms the ability of the proposed kinetic approach to obtain some details of the molecular architecture of non-linear polymers.

Figure 2(a) shows bimodal chromatograms due to the formation of a polymer population at a low concentration but high molecular weight in ATRP of MMA/EGDMA. Notice that this observation is only possible using a SEC/RI/MALLS system. Time evolutions of the molecular architectures of highly branched samples are compared in Figure 2(b). In this figure it is possible to observe the gradual shift of the molecular architecture of branched copolymers away from the one of linear polymers. It is also possible to conclude that erroneous interpretations of chromatograms of non-linear polymers will result from using molecular weight calibrations based upon linear polymers, as before shown in the framework of FRP systems (Gonçalves et al., 2007).

Conclusions

It is shown that important features of the molecular architecture of ATRP synthesized MMA/EGDMA branched copolymers can be measured using a SEC/MALLS system. A general kinetic approach was also used to predict some structural properties of these materials, namely their z -average radius of gyration. The experimental results of this work agree with those found in a comparable research on polyacrylate networks (Gao et al., 2007, 2008) which have also detected the effect of intramolecular cyclizations at a comparable dilution ratio. Reaction runs in bulk are planned to be carried out at a short term and they should yield a more complete assessment on the possibilities of this synthetic method to prepare well defined hyperbranched polymers and networks with few intramolecular loops. The interest of such polymers as building blocks for advanced materials with applications in electronics and in biomedicine/pharmacy is one of the main driving forces for such efforts. The availability of the computing tools to predict the formation and final structure of these complex materials (such as the radius of gyration in sol) despite the huge number of reactions strongly enhances the possibilities of better design of the involved products and processes.

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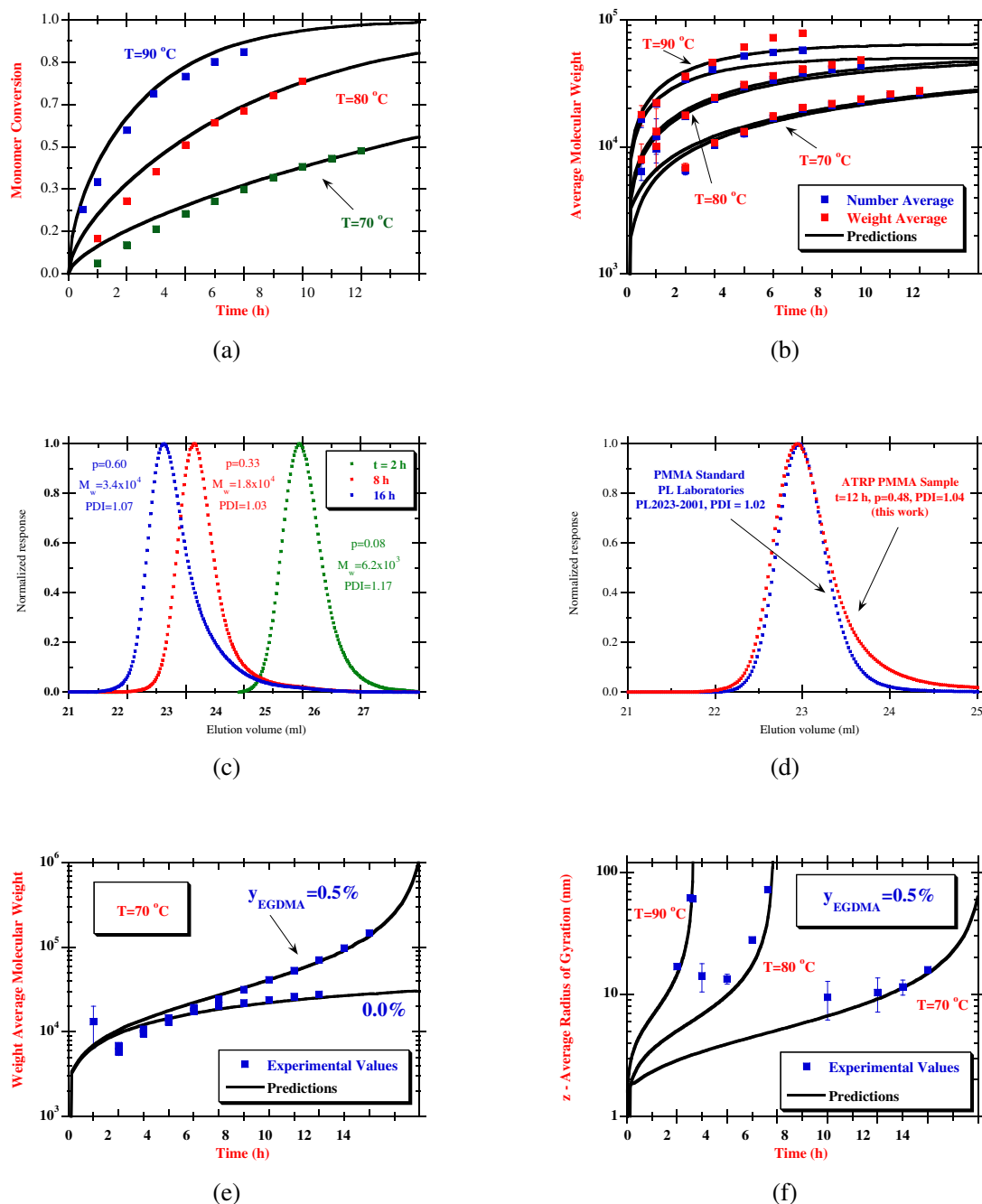


Figure 1: (a) Predictions and experimental observations for monomer conversion in ATRP copolymerizations of MMA/EGDMA at different temperatures. Initial molar ratio MBPA/CuBr/HMTETA=1/1/1 in all runs. (b) Predictions and experimental observations of \overline{M}_n and \overline{M}_w in linear ATRP polymerizations of MMA ($y_{EGDMA} = 0.0\%$) at different temperatures. Experiments at 50 % dilution. (c) RI chromatograms of ATRP synthesized PMMA at 80 °C . Samples with different times of polymerization showing the living character of the polymerization (increase of molecular weight MW without a concomitant increase of PDI). Polymerizations in MMA/Toluene solution (35 % v/v) with initial molar ratios MMA/MBPA=500 and MBPA/CuBr/HMTETA=1/1/1. (d) Comparison of the RI chromatograms of PMMA samples: commercial standard and ATRP synthesized. (e) Predicted and observed time evolution of \overline{M}_w in linear and crosslinked polymers obtained in the ATRP copolymerization of MMA/EGDMA at 70 °C. (f) Predicted and experimentally observed influence of the temperature on \overline{R}_g in ATRP copolymerizations of MMA/EGDMA with constant mole fraction of crosslinker ($y_{EGDMA} = 0.5\%$). Experiments at 50 % dilution.

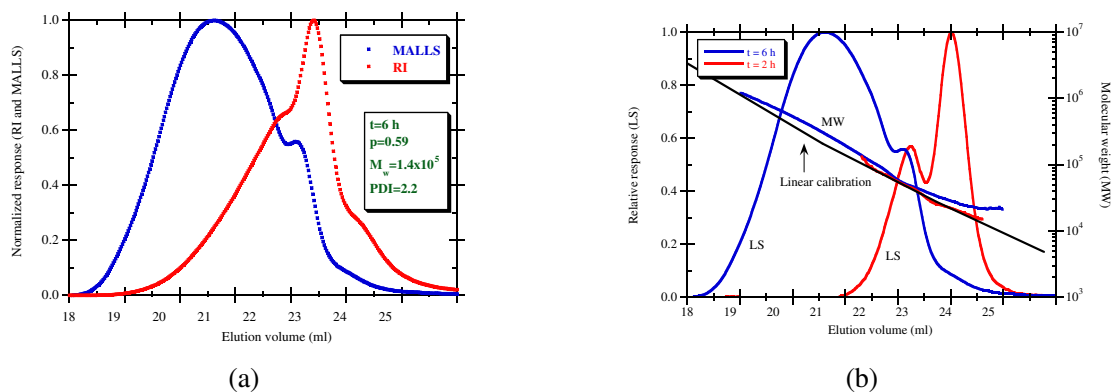


Figure 2: (a) MALLS and RI chromatograms of MMA/EGDMA sample synthesized using ATRP at 90 °C . Copolymerization MMA/EGDMA was performed with 0.5% mole fraction of EGDMA. (b) Molecular weight along SEC chromatogram of MMA/EGDMA samples synthesized using ATRP at 90 °C .

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