Study on the molecular weights of atom transfer radical polymerization of MA and MMA.

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Introduction

Atom transfer radical polymerization is one of the most effective systems in controlling the polymerization of styrenes, acrylates and methacrylates with transition metals catalyst such as cupper, ferric, nickel, cobalt [1-2]. Numbers of block copolymers with a well-controlled architecture have been synthesized [3-4]. In atom transfer radical polymerization the molecular weight and its distribution is considered very important. In this study, theoretical molecular weights of copolymers of methyl acrylate and methyl methacrylates synthesized by atom transfer radical polymerization (ATRP) with a chlorinate telomer of vinyl acetate as the initiator are reported.

Experimental sections

Materials. Methyl acrylate (MA) (Merck, 99.9%), methyl methacrylate (MMA) (Merck, 99.9%) and CuCl (Merck, 97%) were purified [5]. PMDETA (Merck, 99.8%) and tetrahydrofuran (THF) were used as received. Telomer (PVAc-CCl_3) was synthesized in our laboratory [5].

Atom transfer radical polymerization. A required amount of CuCl catalyst was introduced into a glass tube with a magnetic stirrer and the system was degassed with a cycle of vacuum-argon for three times. The mixtures containing MA, MMA, macroinitiator and ligand (PMDETA) were degassed by nitrogen purging before transfer to the glass tube. To remove oxygen from the reaction mixture the freeze–pump–thaw cycle was carried out three times. The tube was immersed in a preheated oil bath at a desired temperature. The reaction mixture was dissolved in THF, filtered and dried for calculation of conversion [6].

Characterization. Molecular weights were measured by a Waters 150C gel permeation chromatography (GPC) equipped with a refractive index detector and a 10^4, 10^3 and 500 °A set of ultrastyrogel columns in THF and 1ml/min at 35 °C.

Results and Discussion

In copolymerization of methyl acrylate (MA) and methyl methacrylate (MMA) with various ratios of MA to MMA and [CuCl]/[PMDETA]/[PVAc-CCl_3] catalyst system in bulk at 80 °C via ATRP, several terpolymer with different copolymer composition, were synthesized. In Table 1 the copolymer compositions (F_1) were calculated with equation 1 and from ^{1}H NMR spectra. In Fig.1 ^{1}H NMR spectra of the PVAc-b-(PMA-co-PMMA) terpolymer is reported. The signals at 0.7-1.2 ppm (l) are assigned to methylene protons (-CH_3) in the MMA monomer unit and the broad signals at 2.4 ppm (f) and 4.2 ppm (g) are assigned to methin (C-H) proton for MA monomer unit in terpolymer.

$$F_1 = \frac{I_{CH(2.4)} + I_{CH(4.2)}}{\langle \frac{I_{CH_3(0.7-1.2)}}{3} + I_{CH(2.4)} + I_{CH(4.2)} \rangle} \qquad \text{Eq. 1}$$

In these reactions at moderately low conversion, theoretical average number molecular weights are calculated with equation 2.

$$M_{n,theo.} = M_{n,Macroinitiator} + Conv. \times F_1 \times M_{MA} + Conv. \times (1 - F_1) \times M_{MMA}$$

Eq. 2

In this equation $M_{n,macroinitiater}$, M_{MA} and M_{MMA} are molecular weights of macroinitiator (2432 gr/mol), MA (86.09 gr/mol) and MMA (100.12 gr/mol) monomers. The average number molecular weight of terpolymer changed with composition of MA and MMA monomers and conversion. The theoretical M_n decreased with an increasing of composition of MA monomer in terpolymers and decreasing of conversion. The experimental and theoretical values of number average molecular weights from GPC and ^{1}H NMR experiments indicated from equation 2 are shown in table 1. The molecular weight distributions of the synthesized block terpolymers were narrowed from 1.77 in macroinitiator to a bout (1.2-1.4) in terpolymers as shown in Table 1. A continuous exchange reaction in atom transfer radical polymerization has been suggested for this observation [1].

Table 1. Atom transfer radical polymerization of MA-MMA in bulk at 80 °C.

Sample no.	f_1	F_1	Conv. %	$M_{n,theo.}$ gr/mole	$M_{n,GPC}$ gr/mole
1	0.438	0.267[1]	19	4274[2]	4388
2	0.56	0.381	16	3959	4064
4	0.825	0.642	11.6	3500	3237
5	0.895	0.796	10.15	3346	2861

f_1 and F_1 are mole fraction of MA in feed and copolymer. $[MA]_0/[Ligand]_0/[CuCl]_0/[PVAc\text{-}CCl_3]_0$=100/2/1/1.

For macroinitiator M_n=2432 gr/mole and PDI=1.77.

1: F_1 = (2.372+0.271) / [(11.437+9.498+0.858)/3 + 2.372+0.271] = 0.267

2: $M_{n\text{-}theo}$ = 2432 + 0.19×0.267×86.09 + 0.19×(1-0.267)×100.12 =4274 gr/mol

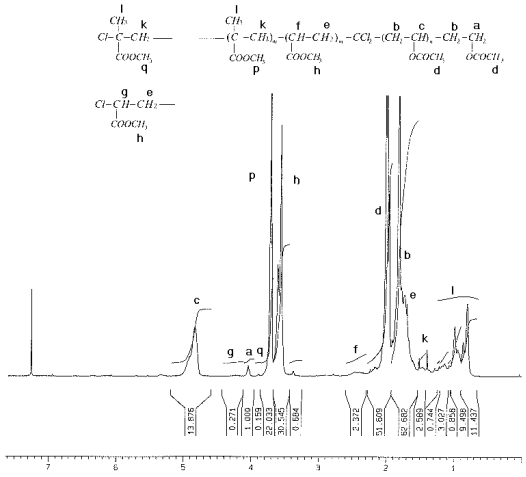

Figure 1. ^{1}H NMR spectra of the PVAc-b-Poly(MA-co-MMA) terpolymers prepared by ATRP

4. Conclusion

The atom transfer radical copolymerization of MA and MMA with macroinitiator, is very sensitive to molecular weight and its distribution. In this work it was possible to calculate the molecular weight of the terpolymers and show that it is close to the experimentally determined number average molecular weight from GPC. The novel block terpolymers showed further narrowing of the polydispersity (1.2-1.4) which is of interest in further molecular design works.

5. Reference

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