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Controlled Radical Polymerization of Furfuryl Methacrylate

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Summary: Atom transfer radical polymerization provides a new method of controlled radical polymerization. The most important advantage of ATRP is that it is tolerant to the different functional groups present in the initiator as well as in the monomer. Furfuryl Methacrylate (FMA) is a specialty monomer, which has applications in coatings, adhesives and in biomedicals. Conventional radical polymerization of FMA leads to excessive gel formation, which limits its applications. In this investigation homo and co-polymerization of FMA has been carried out via ATRP. ATRP of FMA was carried out using CuBr as catalyst and 1, 1, 4, 7, 10, 10 hexamethyltriethylenetetramine (HMTETA) as ligand. There was no gel formation during the polymerization. ATRP of FMA was well controlled with a linear increase of molecular weight (Mn) with monomer conversion. The polymers were characterized by using ^{1}HNMR, FT-IR and GPC analysis. Interestingly, it was observed that the furfuryl ring was not affected during polymerization.

Keywords: atom transfer radical polymerization (ATRP); furfuryl methacrylate (FMA); methyl methacrylate (MMA); furan ring

Introduction

Free radical polymerization is one of the most widely used commercial processes for polymer synthesis. The major disadvantage of radical polymerization is the poor control in molecular composition and structure because of unavoidable bimolecular termination between the growing radicals. Recent advances in controlled radical polymerization (CRP) have made it viable for the synthesis of polymer with desirable functionality and well-defined architecture[1]. Among all the CRP methods atom transfer radical polymerization (ATRP) is very promising as it can be applied to a wide range of monomers like (meth)acrylates and styrene derivatives and is tolerant to different functional groups present in monomer as well as in the initiator [2,3]. Furfuryl Methacrylate is a useful monomer, which is being used in coating and biomedical application 4,5. It can also be used to prepare interesting material because of the presence of reactive furfuryl group [6–7]. Conventional radical polymerization of FMA leads to excessive gel formation and insoluble polymer. This limits its application because of very high viscosity 8–1. This investigation reports the homo and copolymerization of FMA by ATRP. In this process there was no gel formation and the resultant polymer was soluble in most of the organic solvents.

Experimental

Materials

Furfuryl Methacrylate (FMA) (Aldrich, USA) was purified under vacuum distillation. CuBr (Aldrich, 98%) was stirred with glacial acetic acid for 12 h, washed with ethanol and diethyl ether, and then dried under vacuum at 75 °C for 3 days. The purified CuBr was stored in a nitrogen atmosphere. Ethyl 2-bromoisobutyrate (EBiB), (Lancaster, 98%), 1, 1, 4, 7, 10, 10 hexamethyltriethylenetetramine (HMTETA)

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(Aldrich, 99%), and all other chemicals were used as received.

Characterization

Molecular weights and molecular weight distributions of the polymers were determined by Size Exclusion Chromatography (SEC) at ambient temperature using a Viscotek GPC equipped with a Viscogel GPC column (model GMHHR-H # 17360) and a refractive index detector (model VE 3580). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 ml/min and calibration was carried out using low polydispersity polystyrene standards. FT-IR spectra were carried out using a Perkin-Elmer spectrophotometer. IR spectra were recorded in the range of 4000 to 400 cm^{-1}. ^{1}HNMR spectra were recorded in a 300 MHZ Brucker NMR spectrophotometer using $CDCl_3$ as solvent.

Polymerization of FMA

All polymerization reactions of FMA were carried out under nitrogen atmosphere. For ATRP reaction, required amount of FMA and toluene were taken in a three-necked round bottom flask equipped with a water condenser in one neck and a silicon rubber septum at the other. Purified CuBr and HMTETA were added to the reaction flask. The reaction was started at 90 °C by adding the initiator EBIB. At different time intervals, the sample was withdrawn and a part of it was used for the gravimetric determination of monomer conversion. The rest of the samples were passed through a column of neutral alumina oxide to remove the Cu catalyst and followed by the analysis via GPC & NMR spectroscopy.

Results and Discussion

The ATRP of FMA was carried out in solution using EBiB as an initiator and CuBr as a catalyst in combination with HMTETA as a ligand at temperature 90 °C. The molar ratio of FMA, EBiB, CuBr, and HMTETA was maintained at 60/1/1/1. Xia and Matyjaszewski [11] reported that the mole ratio of copper to HMTETA at 1:1 was sufficient to achieve maximum rates and control of polymerization. The reaction mixtures were slightly green in color[12] due to the halogen transfer from alkyl halide to Cu (1) forming Cu (11) complex. In these experiments the colourless reaction mixture turned into green at the given reaction condition indicating the formation of Cu^{11} during the polymerization. Figure 1 shows the kinetic plot of the above ATRP system at 90 °C. It indicates ln $(1/1-x)$ increases linearly with increasing reaction time, demonstrating that concentration of the radical species remained constant throughout the reaction.

Figure 2 shows the dependence of molecular weight and molecular weight distributions on the monomer conversion. The observed molecular weight of the PFMA was slightly higher than the theoretical molecular weight. The polydispersity index (PDI) was broad initially but later decreased to relatively narrow molecular weight (1.5). The deviation from the theoretical molecular weight may be due to the inefficient deactivation of a growing radical to the dormant species because of the initial low concentration of Cu^{II} in the reaction medium. The same ATRP reaction was carried out in the presence of $CuBr_2$ (5 wt% with respect to CuBr). Its kinetics plot is shown in Figure 1. As expected the polymerization was slower with respect to the polymerization with only CuBr. There was 48% conversion after 20 h (Table) and the molecular weight and the molecular weight distribution of the final polymer were 7104 ($M_n^{the\circ} = 4800$) and 1.5 respectively. The greater molecular weight of the polymer with respect to the theoretical molecular weight may be due to the the addition of more monomer molecules per activation – deactivation cycle. There may be some discrepancy in determining the molecular weight of PFMA having a long pendant group. However, the linear kinetic plot of ln $(1/1-x)$ vs time and the linear increase of the molecular weight of the polymer with the conversion indicate the polymerization was controlled.

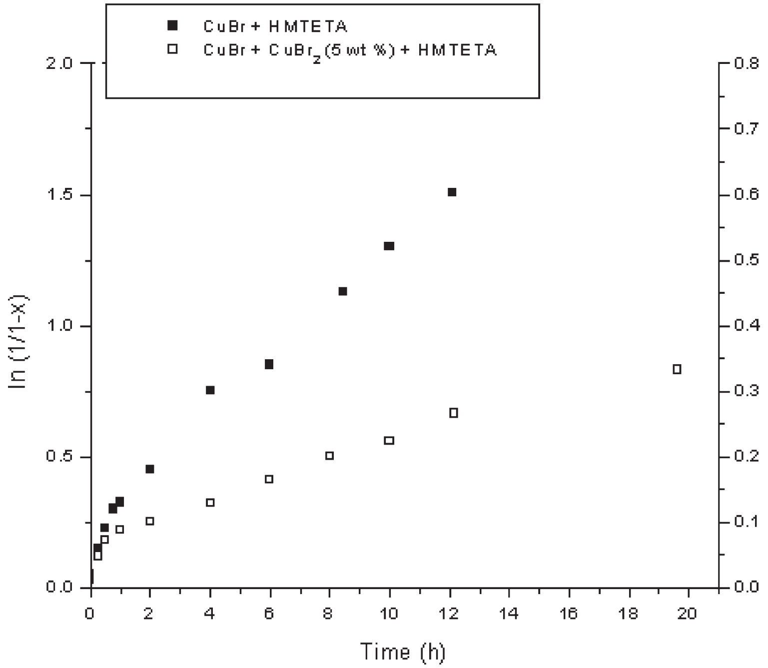

Figure 1.
Kinetic plot of ln [1/(1 − x)] vs. reaction time [CuBr + HMTETA (filled symbols)], [CuBr + CuBr$_2$ (5wt %) + HMTETA (open symbols)], for ATRP of FMA in toluene at 90 °C, [FMA]/ [EBiB]/ [CuBr]/ [HMTETA]: 60/1/1/1.

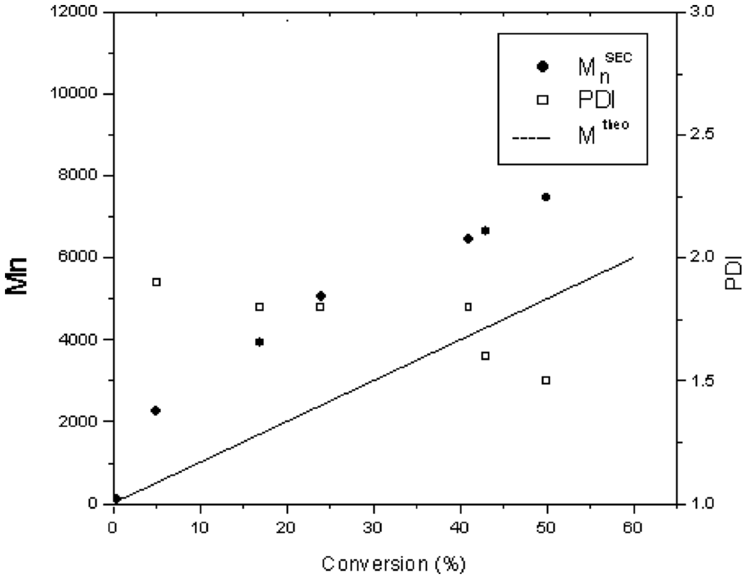

Figure 2.
Plot of M_n (filled symbols) and PDI (open symbols) vs. monomer conversion for ATRP of FMA in toluene at 90 °C, [FMA]/[EBiB]/[CuBr]/[HMTETA]: 60/1/1/1.

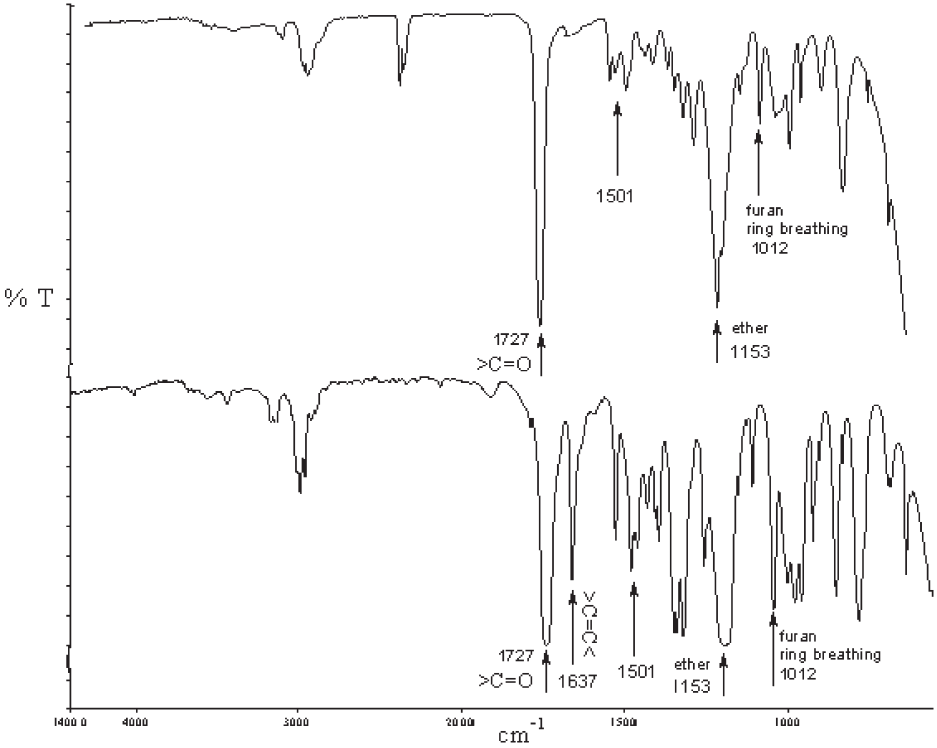

Figure 3.
(a) FT- IR spectra of the Furfuryl Methacrylate monomer and (b) Poly Furfuryl Methacrylate.

The PFMA was characterized by using FT-IR spectroscopy (Figure 3). It indicates that FMA has characteristic peaks at 1727 cm^{-1}, 1637 cm^{-1}, 1153 cm^{-1}, 1501 cm^{-1} and 1012 cm^{-1} due to >C=O and >C=C< group, –C–O– (ether stretching), furan ring stretching and furan ring breathing[13] respectively. In PFMA the peak at

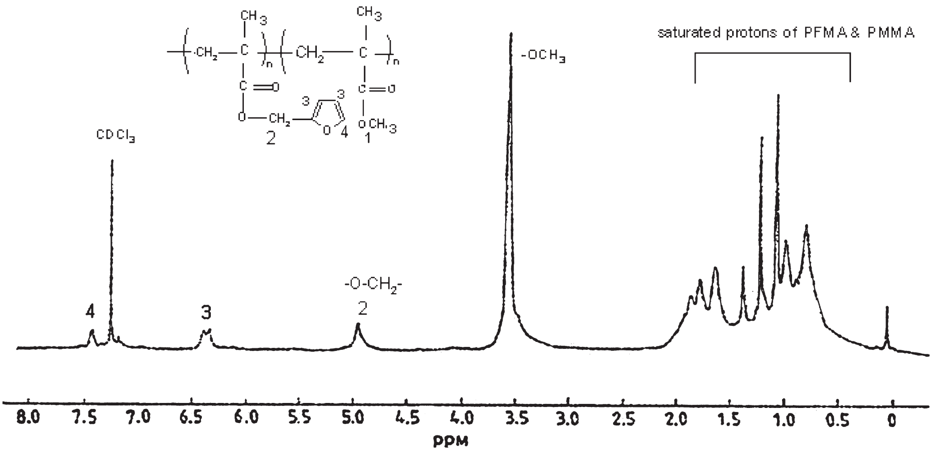

Figure 4.
^{1}HNMR spectrum of poly (methyl methacrylate – co-furfuryl methacrylate) (PMMA-co-PFMA).

Table 1.
Homopolymerization and copolymerization of FMA in toluene via free radical polymerization (FRP) and Atom transfer radical polymerization (ATRP).

Polymer	Method of Polymerization*	Initiating system (Conc. of initiator)	Conv. (%)	Time (h)	Remarks
PFMA	FRP	AIBN (10 mM)	—	6	Insoluble polymer
PFMA	ATRP	EBIB/CuBr/HMTETA (1:1:1) (25 mM)	50	12	Soluble polymer M_n^{SEC} – 7471 MWD - 1.5
PFMA	ATRP	EBIB/CuBr/HMTETA (1:1:1) & $CuBr_2$ (5 wt% w.r.t CuBr) (25 mM)	48	20	Soluble polymer M_n^{SEC} – 7104 MWD - 1.5
(PFMA-co-MMA)	FRP	AIBN (10 mM)	—	6	Insoluble polymer
(PFMA-co-MMA)	ATRP	EBIB/CuBr/HMTETA (1:1:1) (25 mM)	58	12	Soluble polymer M_n^{SEC} – 9500 MWD - 1.6

* FRP and ATRP were carried out at 70 °C and 90 °C respectively.

1637 cm^{-1} disappears indicating C=C has taken part in the formation of polymer. Interestingly, the peaks at 1501 cm^{-1}, 1012 cm^{-1} (furan ring breathing) are not changed indicating the furan ring is not affected during the polymerization. The resultant polymer, PFMA was highly soluble in $CHCl_3$, Toluene and THF, etc.

The copolymerization of FMA and MMA was carried out in toluene using EBIB as initiator CuBr as catalyst in combination with HMTETA as ligand (Table). Figure 4 shows the ^{1}HNMR spectrum of the copolymer of FMA and MMA. The characteristic peaks at 3.5 ppm and 5.0 ppm are due to the $–OCH_3–$ protons in the PMMA part and $–OCH_2–$ proton in the PFMA part. The copolymer composition was calculated from the integrated area of $–OCH_3$ of MMA and $–OCH_2–$ of PFMA. In this case the composition of FMA was calculated to be 23 %. The initial ratio of FMA and MMA was 20:80. The protons at C_3 position of the furan ring appear at 6.4 ppm and the C_4 proton appears at 7.4 ppm. The ratio of the C_3 and C_4 protons were 1:2, it indicates the furan ring was not affected during the ATRP.

Table shows the comparative study of the homo and copolymerization of FMA via conventional free radical polymerization (FRP) and ATRP. All the homo polymers and copolymer of FMA prepared by ATRP were completely soluble in toluene, THF, $CHCl_3$ and in many other organic solvents. In the model experiment, FMA was polymerized in toluene at 70 °C by using azobisisobutryonitrile (AIBN, 10 mM) as an initiator. The resulting polymer was gelled and insoluble in all organic solvents (Table 1). Goiti et al. [8] reported the gel formation during the conventional polymerization of FMA. It was attributed due to the excessive chain transfer involving the C_4 position of the furan ring (chemical structure as shown in Figure 4). In case of ATRP all the homo and copolymers were soluble indicating the side reactions were minized during the polymerization. Most importantly FT-IR and ^{1}HNMR shows the furan ring was not affected during the ATRP.

Conclusion

The homo and copolymerization of FMA was successfully carried out by ATRP using EBIB as initiator, CuBr as catalyst and HMTETA as ligand. The polymerization was controlled with a linear increase of molecular weight and with relatively narrow molecular weight distribution. The polymers prepared by ATRP were completely soluble in organic solvents whereas the polymers prepared by FRP were gelled and were insoluble in organic solvents. The FT-IR and NMR spectra of PFMA showed that the furan ring was not affected during the ATRP. The details of the ATRP of FMA and its application are under progress in our laboratory.

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