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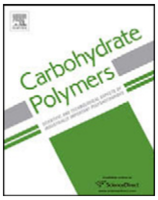

Short communication

Homogeneous grafting poly (methyl methacrylate) on cellulose by atom transfer radical polymerization

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ABSTRACT

Methyl methacrylate (MMA) was homogeneous-grafted on a cellulose based macro-initiator, cellulose chloroacetyl chloride by the atom transfer radical polymerization (ATRP) at a mild reaction temperature. The synthesized cellulose graft copolymers were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopies. The linear first-order kinetics of monomer conversion was determined by headspace gas chromatography. The molecular weights and their distributions of the poly (methyl methacrylate) (PMMA) grafted onto the cellulose backbone were determined by gel permeation chromatography. The results confirmed that the generation of the cellulose grafted PMMA at 50 °C in the given solvent system was a controlled/living ATRP process.

1. Introduction

Cellulose, the most abundant natural material on earth, is mainly used to produce paperboard and paper. However, modification of cellulose by grafting other molecules or special functional groups on its structure allows the material to have more flexible properties, opening the way to many advanced applications (Bianchi, Bonazza, Marsano, & Russo, 2000; Bianchi, Marsano, Ricco, & Russo, 1998; Castellano, Gurruchaga, & Goni, 1997; Farag, Eljazi, & Afaleq, 2002; Hu, 2008; Lonberg, Zhou, Brumer, & Teeri, 2006).

In order to obtain these cellulose-based materials that have the properties of interest, denser or better-defined grafts of predetermined degrees of polymerization are needed. Although the graft copolymerization of various monomers onto cellulose and cellulose derivatives has been carried out by different conventional polymerization techniques, such as ultraviolet light (Shukla & Athalye, 1992), gamma rays (Lu, Yi, Li, & Ha, 2001), plasma ion beams (Sakata & Goring, 1976) and ceric (IV) ion initiation (Gurdag, Guclu, & Ozgumus, 2001) methods, the uncontrolled chain scission makes it impossible to predetermine the length of graft chains on the cellulose backbone. As a result, the concurrent formation of homopolymers and copolymers predominates over graft copolymerization. It was found that grafting vinyl monomers from a mixture of synthetic and natural polymers is an effective solution to overcoming the problems mentioned above. Among many methods for vinyl-related reaction, a radical based controlled/living polymerization, namely atom transfer radical polymerization (ATRP) (Kato, Kamigaito, Sawamoto, & Higashimura, 1995; Wang & Matyjaszewski, 1995), is the most commonly used technique in the cellulose-based grafting polymerization (Matyjaszewski & Xia, 2001). Compared to heterogeneous grafting (Carlmark & Malmstrom, 2002; Hansson, Ostmark, Carlmark, & Malmstrom, 2009), homogeneous grafting polymerization on the cellulose creates more sites and options for introducing novel functional groups, opening new avenues for the design of products, and providing a method to control the total degree of substitution value to obtain a high initiator density.

Since cellulose is insoluble in conventional solvents, the graft polymerization via ATRP in the homogenous case has been mainly limited to cellulose derivatives, such as hydroxypropyl cellulose, ethyl cellulose and cellulose diacetate (Emma, Simon, Karen, & Eva, 2007; Shen, Yu, & Huang, 2005; Vicek, Janata, Latalova, & Kriz, 2006) that are soluble in the common ATRP solvents. Homogeneous grafting polymerization on natural cellulose would undoubtedly give the material properties that are not available in those derived from cellulose derivatives (Krassig & Stannett, 1965).

Since natural cellulose can be dissolved in ionic liquids (IL) (Richard, Scott, John, & Robin, 2002), efforts have been made to synthesize cellulose-based macro-initiators by grafting polymerization via ATRP in IL media (Lin, Zhan, & Liu, 2009; Meng, Gao, Zhang, & Yuan, 2009; Sui, Yuan, Zhou, & Zhang, 2008). However, IL are very expensive to purchase and difficult to recycle, thus limiting their further development for the commercial applications. The dimethylacetamide/lithium chloride (DMAc/LiCl) solvent system, which is much cheaper than IL, has been found to be a good media for dissolving cellulose (Turbak, Kafrawy, & Snyder, 1981).

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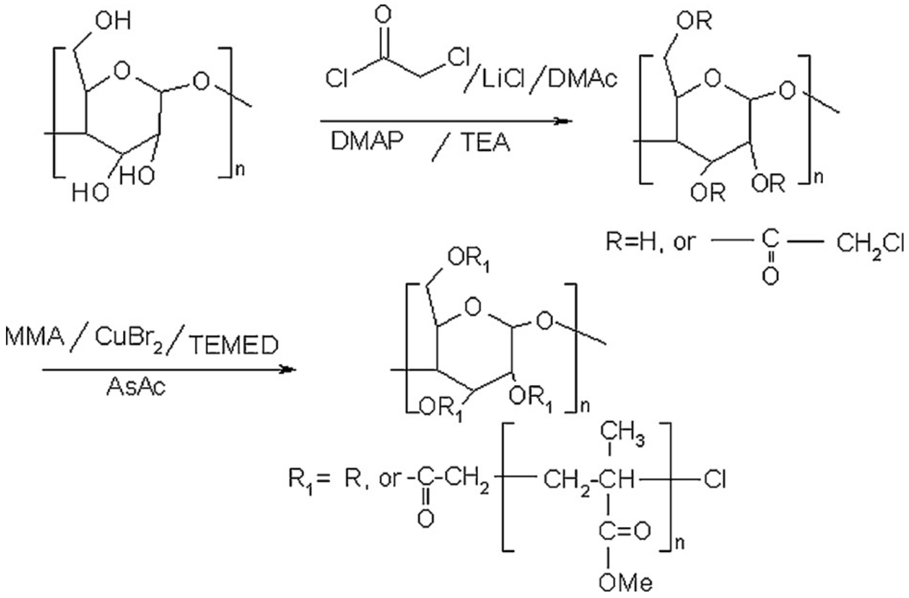

Scheme 1. Synthesis of the cellulose-graft-PMMA copolymer.

Some researchers (Chang, Yamabuki, Onimura, & Oishi, 2008) conducted a work on a PMMA-grafted-cellulose reaction via ATRP at a temperature of 130 °C in such a medium. Possibly, the reaction performed at a high temperature increases the risk of thermally self-initiated polymerization (Greham & Brian, 1993; Xu, Xu, Lu, & Xia, 2007), so that homo- and co-polymerizations might concurrently occur. Because the solubility of the products is poor in common deuterated solvents, it is difficult to obtain the monomer conversion data though NMR analysis. Thus, even if the molecular weight of the polymer bound to the cellulose can be determined by gel permeation chromatographic methods (GPCs), this data alone cannot ensure that the reaction is a fully controlled/living ATRP process.

In this work, we conducted a homogeneous synthesis of MMA grafted on cellulose in DMAc at a mild temperature. The focus was on the characterization and analysis of the synthesis copolymer structure, monomer conversion based on the headspace gas chromatographic (HS-GC) method we newly developed (Zhong, Chai, Qin, & Fu, 2011) and actual polymer molecular weight, in order determine whether the reaction was a controlled/living ATRP process.

2. Experimental

2.1. Materials

All chemicals were purchased from the commercial sources. The MMA was passed though a column of basic Al_2O_3 to remove the inhibitor.

2.2. Synthesis of cellulose chloroacetyl chloride initiators (Cell-ClAc) and ATRP of MMA

2.2.1. Dissolution of cellulose

A mixture of cellulose (3 g, 18 mmol of anhydrous glucose unit), LiCl (7.2 g) and DMAc (80 ml) was heated at 130 °C for 1.5 h in a three-neck flask equipped with a short path Graham condenser and a mechanical agitator (200 rpm) and maintained under an inert N_2 atmosphere.

2.2.2. Acetylation of cellulose

Chloroacetyl chloride, 4-dimethylaminopyridine, and triethylamine in 10 ml of DMAc were added dropwise over a 20 min period to the cellulose solution that was in an ice/water bath. Then the reaction mixture was left in a constant temperature bath at 50 °C for 5 h. The products were purified and vacuum-dried.

2.2.3. ATRP of MMA on cellulose

Cell-ClAc was used to initiate the polymerization of MMA on the cellulose, with $CuBr_2$/N,N,N′,N′-tetramethylethylenediamine (TEMED)/ascorbic acid (AsAc) as a catalyst system, where $[I]/[CuBr_2]/[TEMED]/[AsAc]/[MMA] = 1:0.1:1:1:100$ ([I], moles of chloroacetate group, calculated from the ^1H NMR spectrum of Cell-ClAc).

2.3. Characterizations and analyses

The samples were measured by Fourier transform infrared (FT-IR) spectra (GX Infrared spectrophotometer, PE Company, USA) and nuclear magnetic resonance spectroscopy (NMR) (AVANCE Digital 400 MHz, Bruker, German). The degree of substitution (DS) of Cell-ClAc was obtained from the ^1H NMR.

The monomer conversion during the reaction was measured by the HS-GC method we developed recently (Zhong et al., 2011). The molecular weight and molecular weight distributions (M_w/M_n) of PMMA on the cellulose were determined by GPC (Lin et al., 2009).

3. Results and discussion

3.1. Synthesis of macro-initiator Cell-ClAc and Cell-graft-PMMA

The synthesis of the cellulose-based macro-initiator Cell-ClAc (intermediate product) and Cell-ClAc graft MMA polymerization (final product) were carried out according to the procedures shown in Scheme 1.

As previously reported (Kamigaito, Ando, & Sawamoto, 2001; Mehmet & Mehmet, 2005), the chloroacetyl groups in the Cell-ClAc were the effective initiator sites for the ATRP of MMA. As mentioned above, a higher reaction temperature will increase the risk of the homo-polymerization between monomers. Some researchers (Greham & Brian, 1993; Xu et al., 2007) found that the self-initiated

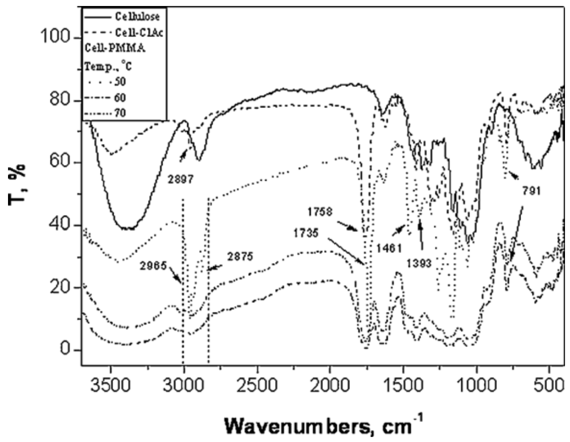

Fig. 1. The FT-IR spectra of pure cellulose, macro-initiator Cell-ClAc and Cell-graft-PMMA.

homo-polymerization of MMA took place at a temperature above 80 °C in both the conventional batch emulsion polymerization and in the ATRP system. Thus, we conducted the ATRP of MMA on Cell-ClAc initiator at 50–70 °C in the DMAc solvent. The functional groups and structures of the products were examined by FT-IR and ^{1}H, ^{13}C NMR.

3.2. Identification and characterization of the structures of intermediate and final products

3.2.1. FT-IR analysis of Cell-ClAc and Cell-PMMA

Fig. 1 shows the FT-IR spectra for the cellulose, Cell-ClAc, and Cell-graft-PMMA products obtained at different reaction temperatures. The presence of two new bands at 1758 and 791 cm^{-1} in the spectrum of Cell-ClAc are attributed to C=O stretching and C–Cl stretching, indicating that the chloroacetyl group has been bonded on the cellulose after homogeneous chloroacetylation. Also, the broad stretching band of hydroxyl groups at 3500 cm^{-1} found in the pure cellulose is significantly reduced in the Cell-ClAc spectrum, indicating that these groups have been partially substituted by the acylation.

The IR spectra of Cell-graft-PMMA shown in Fig. 1 show that there is a shift of the peak at 1758–1735 cm^{-1}, attributed to –C=O in the ester group. In addition, the absorption peaks of the C–H stretching frequencies of the –CH$_2$ and –CH$_3$ groups and the bending modes of the C–H bonds in –CH$_3$ at 2875, 2965, 1461 and 1393 cm^{-1}, respectively, were distinctly observed, indicating that PMMA was chemically bonded on the cellulose. Note that the intensities of the signals of the bands in these ranges for the product samples generated at 60 and 70 °C are much weaker than those for the products formed at 50 °C, indicating that the MMA grafting polymerization on cellulose is more efficient at the lower reaction temperature. This observation also suggests that there is a high possibility of homo-polymerization between MMA monomers even at a temperature as low as 60 °C.

3.2.2. NMR analysis of Cell-ClAc and Cell-PMMA

The introduction of chloroacetyl groups on cellulose with ClAc was further confirmed by ^{1}H NMR and ^{13}C NMR measurements. As shown in Fig. 2a, there appears a new single peak at 4.21 ppm (peak a) for methylene protons in the ester of group of ClAc.

In the ^{13}C NMR spectrum of the methyl carbon in Cell-ClAc (Fig. 2b), the chemical shift of carbonyl carbon appears in the range of 166–170 ppm (besides the multiple peaks instead of the signal peak), indicating that the ClAc substitution on the different hydroxyl groups of cellulose has been achieved, similar to that reported previously (Lin et al., 2009).

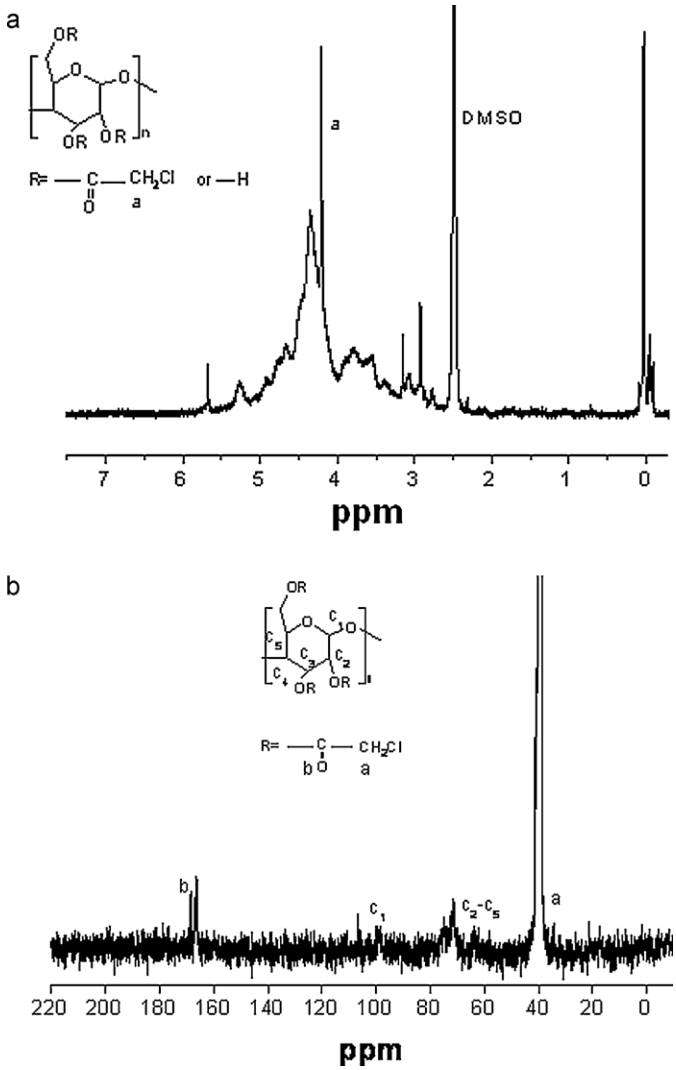

Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of Cell-ClAc (DS = 0.76) in DMSO-d$_6$.

The structure of the graft copolymers Cell-PMMA obtained at a reaction temperature of 50 °C was also characterized by ^{1}H NMR analysis (Fig. 3). The chemical shift of the proton at 3.6 ppm (peak c)

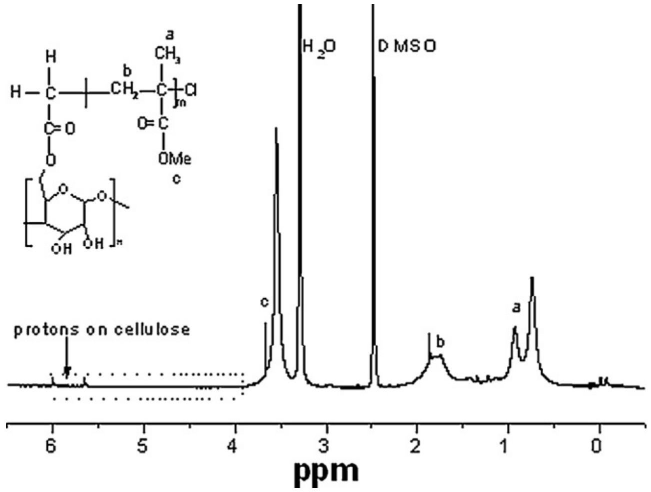

Fig. 3. ^{1}H NMR spectra of Cell-PMMA in DMSO-d$_6$.

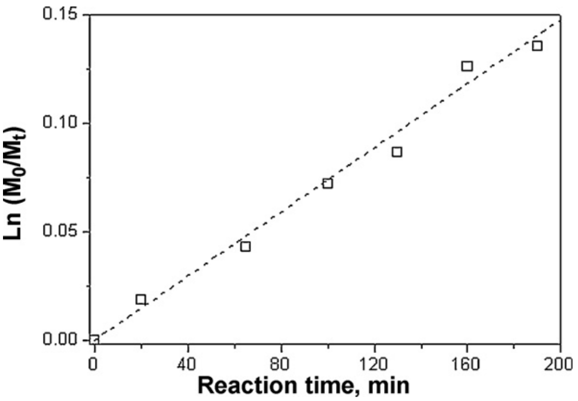

Fig. 4. Semilogarithmic plot of monomer consumption versus time for MMA polymerization.

is attributed to protons of $-OCH_3$ in PMMA, which is evidence that the MMA monomers have been successfully attached to the cellulose backbone. It should be pointed out that although the strong signal of $-OCH_3$ can be used to calculate the number of the PMMA chains, the proton signal of the cellulose backbone is weak, thus the integration of the hydrogen for the cellulose backbone is inaccurate. As a result, it is difficult to obtain the accurate monomer conversion data though NMR analysis.

3.3. Confirmation of ATRP in Cell-graft-PMMA process

As reported previously (Matyjaszewski & Thomas, 2002), the controlled/living of radical polymerization can be identified by linear first-order kinetics, i.e., $\ln(M_0/M_t) = kt$, where M_0 and M_t are the amount of the monomer in the initial solution and at the reaction time t, respectively.

Fig. 4 shows a plot of $\ln(M_0/M_t)$ versus the reaction time during the MMA copolymerization using the Cell-ClAc macro-initiator, which is based on the monomer conversion data measured by the HS-GC technique described previously (Zhong et al., 2011). Clearly, the variation of $\ln(M_0/M_t)$ is linear with time throughout whole reaction period ending at 190 min, indicating a first order reaction, i.e., a controlled/living ATRP process. At the end of the graft polymerization in the solvent system, the reaction medium was also examined and revealed no evidence of homopolymer in the DMAc solvent.

The changes in the molecular weight and the distribution of molecular weights of the grafting copolymer during the reaction measured by GPC can also reveal evidence of an ATRP process (Matyjaszewski & Thomas, 2002) and the results are shown in Fig. 5. Clearly, the molecular weights of the graft PMMA chains that were hydrolyzed from the Cell-PMMA increased linearly with the monomer conversion, and the polydispersity is almost constant and in a relative narrow distribution throughout the process. These results further confirm that the reaction in the present system is a controlled/living ATRP process.

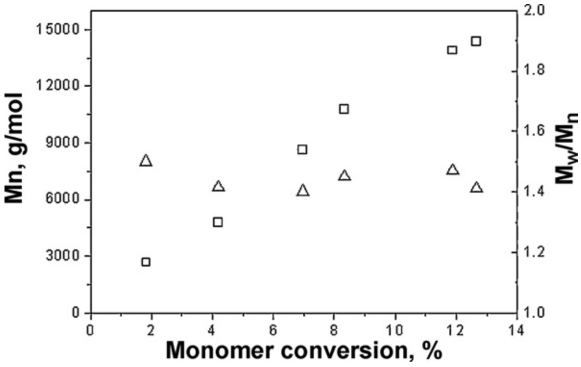

Fig. 5. Dependence of the number average molecular weight (Mn, □) and polydispersities (M_w/M_n, △) of side chain PMMA on monomer conversion.

4. Conclusions

The ATRP of MMA via cellulose based macro-initiator was successfully carried out in the homogeneous solvent system. All these results (first-order kinetics determined by HS-GC method and changes in FT-IR, ^{1}H NMR, ^{13}C NMR and GPC measurements) confirmed that the reaction for cellulose grafting MMA at 50 °C in the given solvent system was a controlled/living ATRP process.

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