Tailor-made poly(methyl methacrylate): Synthesis, Characterization and study the microstructures

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by

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1.1. Summary and conclusions:

ARGET ATRP of MMA was successfully carried out at different temperatures (ambient temperature to 70 ˚C) and in four different solvents: DMF, Toluene, MEK and THF using $CuBr_2$/PMDETA as catalyst system and MCP as an initiator. The effect of solvents on the polymerization rate was studied using four different solvents. Among the four solvents at ambient temperature, the highest rate of polymerization was obtained for DMF as evident by the apparent rate constant value. Thus for successful polymerization in solution proper selection of solvent is important. The polymerization system followed the first order reaction as all the kinetic plots were found to be linear and thus eventually establishes the controlled nature of the polymerization. The value of apparent rate constant was determined for particular polymerization from the slop of the kinetic plot and thus used further for the calculation of the activation energies. It has also been observed that apparent rate constants increase linearly with the polymerization temperatures.

The different microstructures present in PMMA prepared via ARGET-ATRP were studied by 1D and 2D NMR spectroscopy. ^1H NMR along with ^{13}C spectra was employed to study the complete structure of PMMA. Different methods of 2D NMR spectroscopy: TOCSY, HSQC and HMBC were recorded to study the correlation between all protons present in same spin state, between protons of methylene group and carbon ^{13}C of *α*-methyl separated by two bonds and multiple bonds. In general, the microstructures of polymer vary with the different technique of preparation of polymer. But the spectra of PMMA prepared via ARGET-ATRP was found to be similar to the one recorded for PMMA prepared via conventional FRP, except the crosspeaks for coupling between *mr* triad of *α*-methyl protons with *mrm* tetrad methylene, coupling between ^{13}C of methylene group of *mrr* tetrad with protons (H_A and H_B) of *rmr* tetrad and coupling between ^{13}C of methylene group of *mrr* tetrad with *rrr* proton in the *mrrr* pentad were not found. Hence, 2D NMR spectrum was found to be helpful to study the homopolymer of PMMA prepared via ARGET-ATRP.

Tri-block copolymer of PEG and PMMA were prepared using PEG as a macroinitiator via ARGET-ATRP at 70 ˚C. The successful incorporation of ATRP initiator into the PEG was confirmed by FT-IR, ^{1}H and ^{13}C NMR and TGA analyses. This bromo functionalized PEG was used for ARGET-ATRP of MMA. The prepared block polymer PEG-*b*-PMMA was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and TGA analyses. FT-IR, ^{1}H & ^{13}C NMR analyses confirmed the successful block copolymerization. The thermal stability of PEG-*b*-PMMA was found to be better than the neat PMMA prepared by ARGET ATRP.

The graft copolymer of Starch onto PMMA was successfully prepared via ARGET-ATRP using $CuBr_2$/PMDETA as the catalyst system and Starch-Br as a macroinitiator. The successful incorporation of ATRP initiator into starch was confirmed by FTIR analysis. Different macroinitiators were prepared varying the composition of starch and other reagents used. The highest rate of graft polymerization was obtained for the macroinitor D as evident by apparent rate constant value. The kinetic plots were prepared by plotting conversion of monomer in percentage against the polymerization time. The graft polymerization system followed the first-order reaction as all the kinetic plots were found to be linear and thus eventually establishes the controlled nature of the polymerization. The macroinitiator and the graft copolymers were characterized by FT-IR and NMR analyses. The thermal property was studied by Thermogravimetric analysis, DSC and the morphological analysis was studied by SEM.

1.2. Potential application and future prospective of this study:

Tailor-made grafting of PMMA on starch via ARGET-ATRP led to a graft block copolymer. This graft block copolymer can be tuned with low Tg acrylates to prepare a thermoplastic elastomer. Also, the resultant polymer contains starch on its backbone. So, proper tuning can lead to a biodegradable thermoplastic elastomer. The polymer can be used for the replacement of synthetic PMMA for different applications such as in the area of medical. An extensive study on mechanical properties can develop material that can be used for variety of applications replacing commercial synthetic PMMA.

ABA type of triblock copolymer of PEG with MMA was also prepared via ARGET ATRP. The thermal degradation temperature of the block copolymer was found to be greater than the PMMA. Thus, proper tuning and thorough investigation of block combination of PEG and MMA chain length can lead to a triblock copolymer to be behaved as a thermoplastic elastomer. Moreover, the block copolymer contains PEG, a biodegradable polymer that can lead to a biodegradable thermoplastic elastomer. This triblock copolymer will find variety of applications specially in the field of medical due to the combinations of unique properties of PEG and MMA such as weatherability, scratch resistance, biodegradability and non-volatile.

ARGET ATRP has become an effective method to develop new polymeric material with new and well-defined structures such as graft, star and block copolymer. This method allows the polymerization of monomer with the use of catalyst in a very low amount even in a ppm level. Another major advantage of the method is the tolerance to excess amount of reducing agent in the system that eliminates the oxygenating species. The use of catalyst in ppm level reduces the cost of the method. Thus, this method can be followed commercially to develop new polymeric material.