ATOM TRANSFER RADICAL POLYMERIZATION OF LAURYL METHACRYLATE USING SINGLE/ FOUR-ARM INITIATOR AND NANOCLAY AS ADDITIVE

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December, 2011

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by

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CERTIFICATE

This is to certify that the thesis entitled **"ATOM TRANSFER RADICAL POLYMERIZATION LAURYL METHACRYLATE USING SINGLE/ FOUR-ARM INITIATOR AND NANOCLAY AS ADDITIVE"** submitted by **Mr. Pravin Kumar Srivastava** to the Indian Institute of Technology, Delhi, for the award of degree of Doctor of Philosophy is a record of bona fide research work carried out by him. Mr. Pravin Kumar Srivastava has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard. This work has not been submitted, in part or full, to any other university or institute for the award of any other degree or diploma.

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ABSTRACT

This thesis deals with the synthesis of poly(lauryl methacrylate) and its copolymers using living/ controlled radical polymerization methods. The thesis describes systematically the effect of length of alkyl group in ligand [N-(n-alkyl)-2-pyridinemethanimine] on the polymerization of LMA monomer in bulk and solution. An attempt has also been made to synthesize PLMA and its copolymers [random or block] using star initiator. The beneficial effect of nanoclay (Cloisite 30B) as additive on the polymerization of lauryl methacrylate was also investigated.

The thesis is divided into six chapters. Chapter 1 gives the introduction and literature survey. In the chapter 2 of the thesis, we report the effect of length of alkyl group (propyl/hexyl/octyl) in N-(n-alkyl)-2-pyridinemethanimine ligand on the polymerization of LMA monomer in bulk or solution using CuBr as catalyst and EBiB as initiator. The solubility of CuBr in the nonpolar monomer increased in the presence of ligand and was maximum in presence of ligand having longer alkyl side chain. Thus in the presence of N-(n-octyl)-2-pyridinemethanimine (OPMI) ligand, bulk and solution polymerization of LMA was homogeneous even at higher conversions and gave polymers with controlled molecular weight and controlled polydispersity. Living nature of polymerisation was confirmed by the fact that molecular weight increased with increasing percent conversion.

Chapter 3 describes the preparation and characterisation of star-shaped poly(lauryl methacrylate) and polystyrene homopolymer using the "core-first" approach through ATRP. For this purpose, a four arm star initiator "pentaerythritol tetrakis (2- chloro propionate)" was synthesised and characterised using NMR, FTIR and melting point. It was then used as an initiator alongwith CuBr as catalyst and OPMI/PMDETA as ligands to synthesise PLMA/polystyrene homopolymer. Homopolymer was characterused by FTIR, ^{1}H-NMR, GPC. Thermal

characterisation was done using thermogravimetry and differntial scanning calorimetry. Molecular weight of polystyrene determined by GPC was in agreement with the theoretically calculated molecular weight whereas it was higher in case of PLMA. In order to determine the length of arms, polystyrene star polymer was hydrolysed by treating with alcoholic potassium hydroxide and molecular weight of hydrolysed polymer was determined using GPC. It was 1/4th of the original molecular weight which showed that all the four arms are of the same length. This experiment was not possible in case of PLMA as the presence of ester linkage in the side chain of PLMA also gets hydrolysed. Living nature of such polymerisations was investigated by carrying out the chain extension reaction with LMA or styrene monomer. GPC traces shows the monomodal increase in molecular weight which shows living nature of the star-shaped polymer. The molecular weight was also calculated from ^{1}H-NMR and there was a good agreement between the values calculated using NMR and $M_{nGPC.}$ As expected, the viscosity of star-shaped polymers was much lower as compared to linear polymer thus indicating more compact forms of star-shaped polymers than the linear polymer, which may be due to the smaller hydrodynamic radii of star-shaped polymer in solution. Star-shaped polystyrene and PLMA showed two and three step degradation whereas linear homopolymers showed one and two step degradation respectively. The first step degradation observed in the temperature range of 230-240°C was due to the degradation of core. The main degradation steps in star polymers were the same as in linear polymers. Glass transition temperature as determined using DSC showed that star polymers had similar Tg as in linear polymers. Polymer architecture did not show any effect on Tg.

The PS-b-PLMA copolymer and LMA/styrene copolymers were synthesised by ATRP and the details are given in chapter 4. For block copolymers, polystyrene macroinitiator was synthesised

via ATRP using CuBr/ PMDETA as catalyst/ ligand and ethyl-2-bromo-isobutyrate (EBiB) as initiator. Polystyrene thus prepared of varying molecular weight were used as macro-initiators for the polymerization of LMA using CuBr/ OPMI as catalyst/ ligand in toluene at 95°C. The mono-modal molecular weight distribution of the block copolymer obtained using PS macroinitiator shows the better solubility of catalyst complex.

Styrene /LMA copolymer were also synthesized by atom transfer radical copolymerization using LMA and styrene monomer mixture and CuBr/ OPMI/ EBiB as catalyst/ ligand/ initiator. The increase in number average molecular weight with increasing % conversion showed that the system is living. All the polymers synthesized had narrow PDI. Several copolymer were synthesized by varying the molar ratio of monomers in the initial feed and the copolymer composition was determined using ^{1}H-NMR [by taking the ratio of signals at δ=6-7ppm (aromatic protons of styrene) and δ= 3.9 ppm (due to OCH_2 of LMA). From the knowledge of copolymer composition, we calculated the reactivity ratio by computational method using Kelen Tudos method and this was confirmed from nonlinear Error in Variable Model (EVM) program. Thermal characterization of copolymers was done by using differential scanning calorimetry in nitrogen atmosphere. The effect of styrene monomer content on the glass transition temperature of copolymer was investigated by recording DSC scans. Tg increased with increasing amount of styrene. The application of such copolymers as pour point depressant (PPDs) was evaluated in two different base oils having pour point -6°C and -15°C. As the styrene mole fraction in the copolymer increases the solubility of copolymer in the base oil decreases.

In order to see the effect of nanoclay on the controlled polymerization of LMA using CuBr/OPMI/EBiB (catalyst/ligand/initiator), we investigated systematically the effect of nanoclay content and its dispersion time in monomer before polymerization and the details are

included in chapter 5 of the thesis. Polymerization of LMA in presence of varying amounts of nanoclay was done by mixing LMA monomer and 2, 4 and 6% (w/w) of nanoclay and carrying out the polymerization using CuBr/OPMI/EBiB (catalyst/ligand/initiator) initiation system and toluene as solvent at 95°C. Rate of polymerization increased with increasing amounts of nanoclay. In the second set of experiments, we chose 2% nanoclay and it was dispersed in monomer for 0, 10 and 20 h before polymerization. All other conditions were kept constant and kinetics was investigated as a function of dispersion time. Rate of polymerization increased significantly as a function of dispersion time. Rate of polymerization increased with increasing amounts of clay, however PDI also showed an increase whereas increase in dispersion time increased the polymerisation rate without much change in PDI. WAXD and TEM analysis reveals that the nanocomposites prepared by in-situ polymerization showed completely exfoliated clay structures in case of nanocomposites having lower amounts of nano clay whereas in case of samples having higher amounts of nanoclay, mixed morphology was seen i.e. intercalated and exfoliated clay layers. The summary and conclusion are given in chapter 6. Scope for future work is also given.

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